

Chapter 1

Principles of Probability

1. Combining independent probabilities.

You have applied to three medical schools: University of California at San Francisco (UCSF), Duluth School of Mines (DSM), and Harvard (H). You guess that the probabilities you'll be accepted are: $p(\text{UCSF}) = 0.10$, $p(\text{DSM}) = 0.30$, and $p(\text{H}) = 0.50$. Assume that the acceptance events are independent.

- (a) What is the probability that you get in somewhere (at least one acceptance)?
- (b) What is the probability that you will be accepted by both Harvard and Duluth?

- (a) The simplest way to solve this problem is to recall that when probabilities are *independent*, and you want the probability of events A AND B , you can *multiply* them. When events are *mutually exclusive* and you want the probability of events A OR B , you can *add* the probabilities. Therefore we try to structure the problem into an AND and OR problem. We want the probability of getting into H OR DSM or UCSF. But this doesn't help because these events are not mutually exclusive (mutually exclusive means that if one happens, the other cannot happen). So we try again. The probability of acceptance somewhere, $P(a)$, is $P(a) = 1 - P(r)$, where $P(r)$ is the probability that you're rejected everywhere. (You're either accepted somewhere or you're not.) But this probability *can* be put in the above terms. $P(r)$ = the probability that you're rejected at H AND at DSM AND at UCSF. These events are independent, so we have the answer. The probability of rejection at H is $p(rH) = 1 - 0.5 = 0.5$. Rejection at DSM is $p(r\text{DSM}) = 1 - 0.3 = 0.7$. Rejection at UCSF is $p(r\text{UCSF}) = 1 - 0.1 = 0.9$. Therefore $P(r) = (0.5)(0.7)(0.9) = 0.315$. Therefore the probability of at least one acceptance $= P(a) = 1 - P(r) = 0.685$.

(b) The simple answer is that this is the intersection of two independent events:

$$\begin{aligned} p(aH)p(aDSM) &= (0.50)(0.30) \\ &= 0.15. \end{aligned}$$

A more mechanical approach to either part (a) or this part is to write out all the possible circumstances. Rejection and acceptance at H are mutually exclusive. Their probabilities add to one. The same for the other two schools. Therefore all possible circumstances are taken into account by *adding* the mutually exclusive events together, and *multiplying* independent events:

$$[p(aH) + p(rH)][p(aDSM) + p(rDSM)][p(aUCSF) + p(rUCSF)] = 1,$$

or equivalently,

$$\begin{aligned} &= p(aH)p(aDSM)p(aUCSF) + p(aH)p(aDSM)p(rUCSF) \\ &\quad + p(aH)p(rDSM)p(aUCSF) + \dots \end{aligned}$$

where the first term is the probability of acceptance at all 3, the second term represents acceptance at H and DSM but rejection at UCSF, the third term represents acceptance at H and UCSF but rejection at DSM, etc. Each of these events is mutually exclusive with respect to each other; therefore they are all added. Each individual term represents independent events of, for example, *aH and aDSM and aUCSF*. Therefore it is simple to read off the answer in this problem: we want *aH and aDSM*, but notice we don't care about UCSF. This probability is

$$\begin{aligned} p(aH)p(aDSM) &= p(aH)p(aDSM)[p(aUCSF) + p(rUCSF)] \\ &= (0.50)(0.30) \\ &= 0.15. \end{aligned}$$

Note that we could have solved part (a) the same way; it would have required adding up all the appropriate possible mutually exclusive events. You can check that it gives the same answer as above (but notice how much more tedious it is).

2. Probabilities of sequences.

Assume that the four bases A, C, T, and G occur with equal likelihood in a DNA sequence of nine monomers.

- (a) What is the probability of finding the sequence AAATCGAGT through random chance?
- (b) What is the probability of finding the sequence AAAAAAAAAA through random chance?
- (c) What is the probability of finding any sequence that has four A's, two T's, two G's, and one C, such as that in (a)?

- (a) Each base occurs with probability $1/4$. The probability of an *A* in position 1 is $1/4$, of *A* in position 2 is $1/4$, of *A* in position 3 is $1/4$, of *T* in position 4 is $1/4$, and so on. There are 9 bases. The probability of this specific sequence is $(1/4)^9 = 3.8 \times 10^{-6}$.
- (b) Same answer as (a) above.
- (c) Each specific sequence has the probability given above, but in this case there are many possible sequences which satisfy the requirement that we have 4 *A*'s, 2 *T*'s, 2 *G*'s, and 1 *C*. How many are there? We start as we have done before, by assuming all nine objects are distinguishable. There are $9!$ arrangements of nine distinguishable objects in a linear sequence. (The first one can be in any of nine places, the second in any of the remaining eight places, and so on.) But we can't distinguish the four *A*'s, so we have overcounted by a factor of $4!$, and must divide this out. We can't distinguish the two *T*'s, so we have overcounted by $2!$, and must also divide this out. And so on. So the probability of having this composition is

$$\left[\frac{9!}{4!2!2!1!} \right] \left(\frac{1}{4} \right)^9 = 0.014.$$

3. The probability of a sequence (given a composition).

A scientist has constructed a secret peptide to carry a message. You know only the composition of the peptide, which is six amino acids long. It contains one serine **S**, one threonine **T**, one cysteine **C**, one arginine **R**, and two glutamates **E**. What is the probability that the sequence **SECRET** will occur by chance?

The *S* could be in any one of the 6 positions with equal likelihood. The probability that it is in position 1 is (1/6). Given that *S* is in the first position, we have 2 *E*'s which could occur in any of the remaining 5 positions. The probability that one of them is in position 2 is (2/5). Given those two letters in position, the probability that the 1 *C* is in the next of the 4 remaining positions is (1/4). The probability for the *R* is (1/3). For the remaining *E* is (1/2), and for the last *T* is (1/1), so the probability is

$$(1/6)(2/5)(1/4)(1/3)(1/2) = 1/360 = \left[\frac{6!}{1!2!1!1!} \right]^{-1}.$$

4. Combining independent probabilities.

You have a fair six-sided die. You want to roll it enough times to ensure that a **2** occurs at least once. What number of rolls *k* is required to ensure that the probability is at least 2/3 that at least one **2** will appear?

$$q = \frac{5}{6} = \text{probability that a } \mathbf{2} \text{ does not appear on that roll.}$$

$$q^k = \text{probability that a } \mathbf{2} \text{ does not appear on } k \text{ INDEPENDENT rolls.}$$

$$P(k) = 1 - q^k = \text{probability that at least one } \mathbf{2} \text{ appears on } k \text{ rolls.}$$

For

$$\begin{aligned} P(k) &\geq \frac{2}{3}, 1 - q^k \geq \frac{2}{3} \implies q^k \leq \frac{1}{3} \implies k \ln q \leq \ln \left(\frac{1}{3} \right) \\ \implies k &\geq \frac{\ln(1/3)}{\ln(5/6)} = 6.03 \end{aligned}$$

Approximately six or more rolls will ensure with probability $P \geq 2/3$ that a **2** will appear.

5. Predicting compositions of independent events.

Suppose you roll a die three times.

- (a) What is the probability of getting a total of two **5**'s from all three rolls of the dice?
- (b) What is the probability of getting a total of *at least* two **5**'s from all three rolls of the die?

The probability of getting x **5**'s on n rolls of the dice is

$$\left(\frac{1}{6}\right)^x \left(\frac{5}{6}\right)^{n-x} \frac{n!}{x!(n-x)!}$$

Note that this is a “2-outcome” problem (getting a **5** or not getting a **5**). It is not a “6-outcome” problem.

- (a) So the probability of two **5**'s on three dice rolls is

$$\begin{aligned} \left(\frac{1}{6}\right)^2 \left(\frac{5}{6}\right)^1 \frac{3!}{2!1!} &= \left(\frac{1}{36}\right) \left(\frac{5}{6}\right) 3 \\ &= \frac{15}{216} \\ &= 6.94 \times 10^{-2} \end{aligned}$$

- (b) The probability of getting *at least* two **5**'s is the probability of getting two **5**'s or three **5**'s. Since these two situations are mutually exclusive, we seek

$$\begin{aligned} p(\text{two } \mathbf{5}\text{'s}) + p(\text{three } \mathbf{5}\text{'s}) &= \left(\frac{1}{6}\right)^2 \left(\frac{5}{6}\right) \frac{3!}{2!1!} + \left(\frac{1}{6}\right)^3 \left(\frac{5}{6}\right)^0 \frac{3!}{3!0!} \\ &= \frac{15}{216} + \frac{1}{216} \\ &= \frac{16}{216} \\ &= 7.41 \times 10^{-2} \end{aligned}$$

6. Computing a mean and variance.

Consider the probability distribution $p(x) = ax^n$, $0 \leq x \leq 1$, for a positive integer n .

- (a) Derive an expression for the constant a , to normalize $p(x)$.
- (b) Compute the average $\langle x \rangle$ as a function of n .
- (c) Compute $\sigma^2 = \langle x^2 \rangle - \langle x \rangle^2$ as a function of n .

$$\begin{aligned} \text{(a)} \quad \int_0^1 p(x) dx &= 1 \implies \int_0^1 ax^n dx = \left. \frac{ax^{n+1}}{n+1} \right|_0^1 = \frac{a}{n+1} \\ &= 1 \implies a = n+1. \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \langle x \rangle &= \int_0^1 xp(x) dx \\ &= \int_0^1 (n+1)x^{n+1} dx = \left. \left(\frac{(n+1)x^{n+2}}{n+2} \right) \right|_0^1 = \frac{n+1}{n+2}. \end{aligned}$$

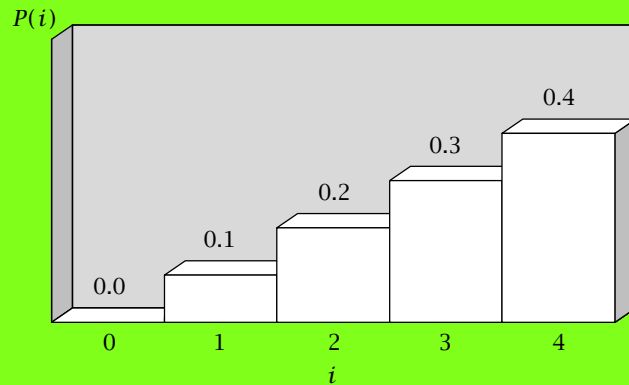
$$\begin{aligned} \text{(c)} \quad \langle x^2 \rangle &= \int_0^1 x^2 p(x) dx \\ &= (n+1) \int_0^1 x^{n+2} dx \\ &= (n+1) \left. \left(\frac{x^{n+3}}{n+3} \right) \right|_0^1 = \frac{n+1}{n+3}. \end{aligned}$$

So

$$\begin{aligned} \sigma^2 &= \langle x^2 \rangle - \langle x \rangle^2 \\ &= \left(\frac{n+1}{n+3} \right) - \left(\frac{n+1}{n+2} \right)^2. \end{aligned}$$

7. Computing the average of a probability distribution.

Compute the average $\langle i \rangle$ for the probability distribution function shown in the figure below.



A simple probability distribution.

$$\begin{aligned}\langle i \rangle &= \sum_{i=0}^4 ip(i) \\ &= 0(0.0) + 1(0.1) + 2(0.2) + 3(0.3) + 4(0.4) \\ &= 3\end{aligned}$$

8. Predicting coincidence.

Your statistical mechanics class has twenty-five students. What is the probability that at least two classmates have the same birthday?

If you first find the probability, q , that no two students have the same birthday, then the quantity you want is

$$p(\text{2 students have same birthday}) = 1 - q$$

The probability that a second student does not have the same birthday as the first is $(364/365)$. The probability that the third student has a birthday different than either of the first two is $(363/365)$, and so on. It is like a sequence problem in which each possible

birthday is one card drawn out of a barrel. The probability that no two people have the same birthday, out of m people, is:

$$q = \left(\frac{364}{365}\right) \left(\frac{363}{365}\right) \left(\frac{362}{365}\right) \cdots \left(\frac{365 - (m - 1)}{365}\right)$$

In factorial notation,

$$q = \frac{N!}{(N - m)!N^m}$$

where $N = 365$. (Incidentally, this expression is identical to the expression for excluded volume in the Flory–Huggins model of polymer solutions (see Chapter 31)). Using Stirling's approximation $x! \approx (x/e)^x$, we get

$$q = \frac{(N/e)^N}{\left(\frac{N-m}{e}\right)^{N-m} N^m}$$

Collecting together terms in e and dividing the numerator and denominator by N^N gives

$$q = \frac{e^{-m}}{\left(1 - \frac{m}{N}\right)^{N-m}}$$

Substituting $m = 25$ students and $N = 365$ gives

$$\begin{aligned} q &= 0.4163, \quad \text{so} \\ p &= 1 - q \\ &= 0.5837 \end{aligned}$$

There is a better than 50% chance two students will have the same birthday!

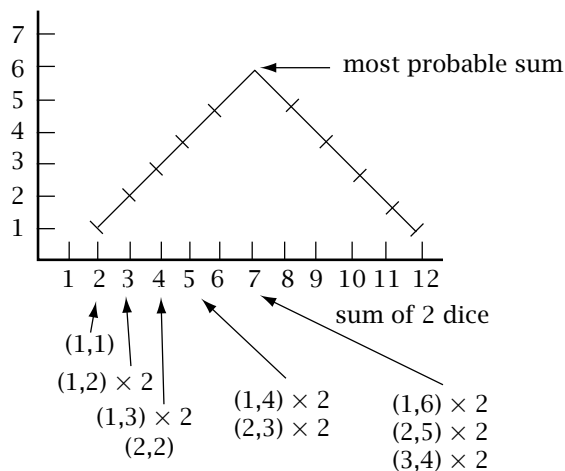
9. The distribution of scores on dice.

Suppose that you have n dice, each a different color, all unbiased and six-sided.

- If you roll them all at once, how many distinguishable outcomes are there?
- Given two distinguishable dice, what is the most probable sum of their face values on a given throw of the pair? (That is, which sum between two and twelve has the greatest number of different ways of occurring?)
- What is the probability of the most probable sum?

- (a)
- | | |
|--------------|--------------|
| 6 | on one die |
| 6×6 | on two dice |
| \vdots | |
| 6^n | on n dice. |

- (b) Number of ways a sum can occur



When dice show different numbers, there is a degeneracy of two. When each of the dice has the same number, the degeneracy equals one.

- (c) probability of 7 = $p(7) = \frac{\text{number of ways of getting 7}}{\text{total number of ways of all outcomes}}$

$$p(7) = \frac{6}{1 + 2 + 3 + 4 + 5 + 6 + 5 + 4 + 3 + 2 + 1} = \frac{1}{6}$$

10. The probabilities of identical sequences of amino acids.

You are comparing protein amino acid sequences for homology. You have a twenty-letter alphabet (twenty different amino acids). Each sequence is a string n letters in length. You have one test sequence and s different data base sequences. You may find any one of the twenty different amino acids at any position in the sequence, independent of what you find at any other position. Let p represent the probability that there will be a ‘match’ at a given position in the two sequences.

- (a) In terms of s , p , and n , how many of the s sequences will be perfect matches (identical residues at every position)?
- (b) How many of the s comparisons (of the test sequence against each database sequence) will have exactly one mismatch at any position in the sequences?

- (a) For comparing one sequence, each position assumed independent, the probability of a perfect match of all n residues is
 $p^n = (\text{number of matched seqs}/\text{number of total seqs}) \implies$
number of matches in s sequences $= sp^n$.
- (b) $n - 1$ positions match, so the probability is p^{n-1} ; one position doesn't match which has the probability $(1 - p)$; and there are n different positions at which the mismatch could occur, therefore

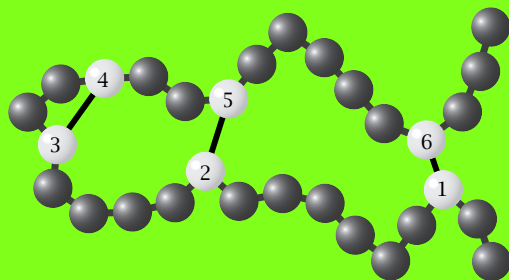
$$= sp^{n-1}(1 - p)n$$

Note in general, for k matches:

$$(1) \quad P(k) = sp^k(1 - p)^{n-k} \frac{n!}{k!(n - k)!}.$$

11. The combinatorics of disulfide bond formation.

A protein may contain several cysteines, which may pair together to form disulfide bonds as shown in the figure below. If there is an even number n of cysteines, $n/2$ disulfide bonds can form. How many different disulfide pairing arrangements are possible?



This disulfide bonding configuration with pairs 1-6, 2-5, and 3-4 is one of the many possible pairings. Count all the possible pairing arrangements.

Number the individual sulfhydryl groups along the chain. The first sulfhydryl along the sequence can bond to any of the other $n - 1$. This removes two sulfhydryls from consideration. The third sulfhydryl can then bond to any of the remaining $n - 3$. Four sulfhydryls are now removed from consideration. The fifth can now bond to any of the remaining $n - 5$ sulfhydryls, etc., until all $n/2$ bonds are formed. Thus the total possible number of arrangements of disulfide bonds is a product of $n/2$ terms:

$$D(n) = (n - 1)(n - 3)(n - 5) \cdots 1$$

Another approach gives an expression that is easier to calculate. Consider placing the sulfhydryls in a sequence. The first place may be occupied by any of n sulfhydryls, the second place by any of $n - 1$ sulfhydryls, the third by any of $n - 2$ sulfhydryls, etc. Thus if each sulfhydryl were distinguishable from every other, there would be $n!$ arrangements. However, each sulfhydryl has a mate from which it cannot be distinguished. We must divide by a factor of 2 (per bond) to correct for the indistinguishability of the two ends of each bond. Finally, since we cannot distinguish any of the $n/2$ bonds from any other, we must also divide by $(n/2)!$. Hence the number of arrangements is

$$W(n) = \frac{n!}{2^{n/2} \left(\frac{n}{2}\right)!}.$$

Although these two equations were derived in very different ways, they are numerically identical for all n .

12. Predicting combinations of independent events.

If you flip an unbiased green coin and an unbiased red coin five times each, what is the probability of getting four red heads and two green tails?

The probability of four red heads in five coin flips is

$$\left(\frac{1}{2}\right)^5 \left(\frac{5!}{4!1!}\right) = \frac{5}{32}.$$

The probability for two green tails is

$$\left(\frac{1}{2}\right)^5 \frac{5!}{2!3!} = \frac{10}{32}.$$

Since the green coin flips are independent of the red coin flips, the probability we seek is $(5/32)(10/32) = (50/1024) = 4.88 \times 10^{-2}$.

13. A pair of aces.

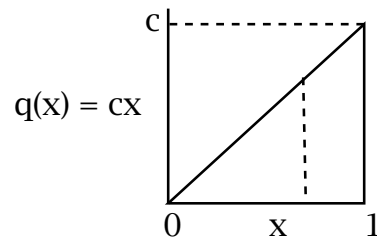
What is the probability of drawing two aces in two random draws without replacement from a full deck of cards?

A deck has 52 cards and four aces. The probability of getting an ace on the first draw is $4/52 = 1/13$. Since you draw without replacement, the probability of getting one of the remaining three aces on the second draw is $3/51$, so the probability of two aces on two draws is

$$\left(\frac{4}{52}\right) \left(\frac{3}{51}\right) = 4.5 \times 10^{-3}.$$

14. Average of a linear function.

What is the average value of x , given a distribution function $q(x) = cx$, where x ranges from zero to one, and $q(x)$ is normalized?



$$\begin{aligned}\langle x \rangle &= \int_0^1 x q(x) dx = \int_0^1 cx^2 dx \\ &= c \left(\frac{x^3}{3} \right)_0^1 = \frac{c}{3}\end{aligned}$$

We can also find c :

$$\begin{aligned}1 &= \int_0^1 q(x) dx = \int_0^1 cx dx \\ &= \left(\frac{cx^2}{2} \right)_0^1 = \frac{c}{2} = 1\end{aligned}$$

So,

$$\begin{aligned}c &= 2 \\ \langle x \rangle &= \frac{c}{3} = \frac{2}{3}\end{aligned}$$

15. The Maxwell-Boltzmann probability distribution function.

According to the kinetic theory of gases, the energies of molecules moving along the x -direction are given by $\varepsilon_x = (1/2)mv_x^2$, where $m =$ mass and v_x is the velocity in the x -direction. The distribution of particles over velocities is given by the Boltzmann law, $p(v_x) = e^{-mv_x^2/2kT}$. This is the Maxwell-Boltzmann distribution (velocities may range from $-\infty$ to $+\infty$).

- (a) Write the probability distribution $p(v_x)$, so that the Maxwell-Boltzmann distribution is correctly normalized.
- (b) Compute the average energy $\langle (1/2)mv_x^2 \rangle$.
- (c) What is the average velocity $\langle v_x \rangle$?
- (d) What is the average momentum $\langle mv_x \rangle$?

According to the kinetic theory of gases, the energies of molecules along the x -direction are given by $\varepsilon_x = (1/2)mv_x^2$, where $m =$ mass and v_x is the velocity in the x -direction. Their distribution is given by the Boltzmann law, $e^{-mv_x^2/2kT}$. This is the Maxwell-Boltzmann distribution. (Note that velocities range from $-\infty$ to $+\infty$.)

- (a) To write the probability distribution $p(v_x)dv_x$ so that the Maxwell-Boltzmann distribution is correctly normalized, we require

$$c \int_{-\infty}^{\infty} e^{-mv_x^2/2kT} dv_x = 1$$

From integral tables, we see that

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx = \left(\frac{\pi}{a}\right)^{1/2}.$$

Aside To compute integrals of the form

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx$$

we use the following trick. It is easy to see that we can write

$$I^2 = \int_{-\infty}^{\infty} e^{-ax^2} dx \int_{-\infty}^{\infty} e^{-ay^2} dy = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-a(x^2+y^2)} dx dy$$

This is now an integral over the entire $x - y$ plane. Converting to polar coordinates r and θ and recognizing that $r^2 = x^2 + y^2$, the integral becomes

$$I^2 = \int_0^\infty dr r \int_0^{2\pi} d\theta e^{-ar^2} = \int_0^\infty dr r e^{-ar^2} \int_0^{2\pi} d\theta = 2\pi \int_0^\infty dr r e^{-ar^2}$$

Making the substitution that $u = -ar^2$, $du = -2ar dr$, we can finish the integral

$$I^2 = -\frac{\pi}{a} \int_0^{-\infty} du e^u = -\frac{\pi}{a} e^u \Big|_0^{-\infty} = \frac{\pi}{a}$$

hence

$$I = \left(\frac{\pi}{a}\right)^{1/2}.$$

For our integral, $a = m/2kT$.

$$\int_{-\infty}^\infty e^{-mv_x^2/2kT} dv_x = \left[\frac{2\pi kT}{m}\right]^{1/2} \implies p(v_x) dv_x = \left[\frac{m}{2\pi kT}\right]^{1/2} e^{-mv_x^2/2kT} dv_x$$

(b) To compute the average energy, $\langle \frac{1}{2}mv_x^2 \rangle$, we have

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \int_{-\infty}^\infty \frac{1}{2}mv_x^2 p(v_x) dv_x = \frac{m}{2} \left[\frac{2\pi kT}{m}\right]^{1/2} \int_{-\infty}^\infty v_x^2 e^{-mv_x^2/2kT} dv_x$$

Again consulting our table of integrals, we find

$$\int_{-\infty}^\infty x^2 e^{-ax^2} dx = \frac{\pi^{1/2}}{2a^{3/2}}$$

Aside: Integrals of the form

$$\int_{-\infty}^\infty x^2 e^{-ax^2} dx$$

can be computed by integration by parts. Recall that

$$\int_a^b u dv = uv \Big|_a^b - \int_a^b v du$$

Choosing the substitutions $u = x$ and $dv = xe^{-ax^2}$, then $du = dx$ and $v = -\frac{1}{2a}e^{-ax^2}$. Our integral therefore becomes

$$\int_{-\infty}^\infty x^2 e^{-ax^2} dx = -\frac{1}{2a}xe^{-ax^2} \Big|_{-\infty}^\infty + \frac{1}{2a} \int_{-\infty}^\infty e^{-ax^2} dx = \frac{1}{2a} \left(\frac{\pi}{a}\right)^{1/2} = 0 + \frac{\pi^{1/2}}{2a^{3/2}}$$

Note that we have used the result of the integral from part (a) above.

Therefore

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \frac{1}{2}m \left[\frac{\pi^{1/2}}{2a^{3/2}} \right] \left[\frac{m}{2\pi kT} \right]^{1/2} = \frac{1}{4}m \left[\left(\frac{2kT}{m} \right)^{3/2} \right] \left[\frac{m}{\pi^{1/2}kT} \right]^{1/2} = \frac{1}{2}kT.$$

- (c) To find the average velocity, $\langle v_x \rangle$, we recall that for functions with *odd* symmetry ($f(x) = -f(-x)$), the integral under the curve for negative x cancels with that under the curve for positive x . Using the fact that $p(x) = p(-x)$,

$$\begin{aligned} \langle v_x \rangle &= \int_{-\infty}^{\infty} v_x p(v_x) dv_x \\ &= \int_{-\infty}^0 v_x p(v_x) dv_x + \int_0^{\infty} v_x p(v_x) dv_x \\ &= \int_0^{\infty} (-v_x) p(-v_x) dv_x + \int_0^{\infty} v_x p(v_x) dv_x \\ &= - \int_0^{\infty} v_x p(v_x) dv_x + \int_0^{\infty} v_x p(v_x) dv_x \\ &= 0. \end{aligned}$$

- (d) What is the average momentum, $\langle mv_x \rangle$?

$$\langle mv_x \rangle = m \langle v_x \rangle = 0,$$

from the result above.

16. Predicting the rate of mutation based on the Poisson probability distribution function.

The evolutionary process of amino acid substitutions in proteins is sometimes described by the Poisson probability distribution function. The probability $p_s(t)$ that exactly s substitutions at a given amino acid position occur over an evolutionary time t is

$$p_s(t) = \frac{e^{-\lambda t} (\lambda t)^s}{s!},$$

where λ is the rate of amino acid substitutions per site per unit time. Fibrinopeptides evolve rapidly: $\lambda_F = 9.0$ substitutions per site per 10^9 years. Lysozyme is intermediate: $\lambda_L \approx 1.0$. Histones evolve slowly: $\lambda_H = 0.010$ substitutions per site per 10^9 years.

- (a) What is the probability that a fibrinopeptide has no mutations at a given site in $t = 1$ billion years?
- (b) What is the probability that lysozyme has three mutations per site in 100 million years?
- (c) We want to determine the expected number of mutations $\langle s \rangle$ that will occur in time t . We will do this in two steps. First, using the fact that probabilities must sum to one, write $\alpha = \sum_{s=0}^{\infty} (\lambda t)^s / s!$ in a simpler form.
- (d) Now write an expression for $\langle s \rangle$. Note that

$$\sum_{s=0}^{\infty} \frac{s(\lambda t)^s}{s!} = (\lambda t) \sum_{s=1}^{\infty} \frac{(\lambda t)^{s-1}}{(s-1)!} = \lambda t \alpha.$$

- (e) Using your answer to part (d), determine the ratio of the expected number of mutations in a fibrinopeptide to the expected number of mutations in histone protein, $\langle s \rangle_{\text{fib}} / \langle s \rangle_{\text{his}}$.

- (a) What is the probability that a fibrinopeptide has no mutations at a given site in $t = 1$ billion years?

$$\begin{aligned} P_0(t) &= e^{-\lambda_F t} = \exp(-(9.0 \text{ per } 10^9 \text{ years})(10^9 \text{ years})) \\ &= e^{-9} = 1.23 \cdot 10^{-4}. \end{aligned}$$

- (b) What is the probability lysozyme has three mutations per site in 100 million years?

$$\begin{aligned} \lambda_L t &= (1.0 \text{ per } 10^9 \text{ years})(10^8 \text{ years}) = 0.1 \\ P_3(t) &= \frac{e^{-\lambda_L t} (\lambda_L t)^3}{3!} = \frac{(e^{-0.1})(0.1)^3}{6} \\ &= 1.51 \cdot 10^{-4}. \end{aligned}$$

- (c) We want to know the expected number of mutations $\langle s \rangle$ that will occur in time t . We will do this in two steps. First, using the fact that probabilities must sum to one, write

$$\alpha = \sum_{s=0}^{\infty} \frac{(\lambda t)^s}{s!}$$

in a simpler form. Since the probabilities sum to 1,

$$\sum_{s=0}^{\infty} P_s(t) = \sum_{s=0}^{\infty} \frac{e^{-\lambda t} (\lambda t)^s}{s!} = e^{-\lambda t} \sum_{s=0}^{\infty} \frac{(\lambda t)^s}{s!} = 1$$

Therefore

$$\alpha = \sum_{s=0}^{\infty} \frac{(\lambda t)^s}{s!} = e^{\lambda t}.$$

(d) Now write an expression for $\langle s \rangle$.

Hint: Note that $\sum_{s=0}^{\infty} \frac{s(\lambda t)^s}{s!} = (\lambda t) \sum_{s=1}^{\infty} \frac{(\lambda t)^{s-1}}{(s-1)!} = \lambda t \alpha$

$$\begin{aligned} \langle s \rangle &= \sum_{s=0}^{\infty} s P_s(t) = \sum_{s=0}^{\infty} \frac{s e^{-\lambda t} (\lambda t)^s}{s!} \\ &= e^{-\lambda t} (\lambda t) \sum_{s=1}^{\infty} \frac{(\lambda t)^{s-1}}{(s-1)!} \\ &= e^{-\lambda t} (\lambda t) \sum_{h=0}^{\infty} \frac{(\lambda t)^h}{h!} = (\lambda t \alpha) e^{-\lambda t} \end{aligned}$$

so

$$\langle s \rangle = \lambda t.$$

(e) Using (d), determine the ratio of the expected number of mutations in a fibrinopeptide to the expected number of mutations in histone, $\langle s \rangle_{\text{fib}} / \langle s \rangle_{\text{his}}$.

$$\frac{\langle s \rangle_{\text{fib}}}{\langle s \rangle_{\text{his}}} = \frac{\lambda_F t}{\lambda_H t} = \frac{\lambda_F}{\lambda_H} = \frac{9}{0.01} = 900.$$

17. Probability in court.

In forensic science, DNA fragments found at the scene of a crime can be compared with DNA fragments from a suspected criminal to determine that the probability that a match occurs by chance. Suppose that DNA fragment A is found in 1% of the population, fragment B is found in 4% of the population, and fragment C is found in 2.5% of the population.

- (a) If the three fragments contain independent information, what is the probability that a suspect's DNA will match all three of these fragment characteristics by chance?
- (b) Some people believe such a fragment analysis is flawed because different DNA fragments do not represent independent properties. As before, suppose that fragment A occurs in 1% of the population. But now suppose that the conditional probability of B , given that A is $p(B|A) = 0.40$ rather than 0.040, and $p(C|A) = 0.25$ rather than 0.025. There is no additional information about any relationship between B and C . What is the probability of a match now?

- (a) Since the fragments are independent

$$\begin{aligned} p &= p(A) p(B) p(C) \\ &= (0.01)(0.04)(0.025) = 1 \times 10^{-5}. \end{aligned}$$

- (b)

$$\begin{aligned} p &= p(A) p(B|A) p(C|A) \\ &= (0.01)(0.40)(0.25) = 1 \times 10^{-3}. \end{aligned}$$

18. Flat distribution.

Given a flat distribution, from $x = -a$ to $x = a$, with probability distribution $p(x) = 1/(2a)$:

- (a) Compute $\langle x \rangle$.
- (b) Compute $\langle x^2 \rangle$.
- (c) Compute $\langle x^3 \rangle$.
- (d) Compute $\langle x^4 \rangle$.

- (a) $\langle x \rangle = \int_{-a}^a xp(x) dx = \int_{-a}^a \frac{x}{2a} dx = \int_0^a \frac{x}{2a} dx - \int_0^a \frac{x}{2a} dx = 0.$
- (b) $\langle x^2 \rangle = \int_{-a}^a x^2 p(x) dx = \left(\frac{1}{2a} \right) \left(\frac{x^3}{3} \right) \Big|_{-a}^a = \frac{1}{2a} \left[\frac{a^3}{3} - \left(-\frac{a^3}{3} \right) \right] = \frac{a^2}{3}.$
- (c) By symmetry (as in (a)), $\langle x^3 \rangle = 0$. In fact $\langle x^n \rangle = 0$ for all odd integers, n .
- (d) $\langle x^4 \rangle = \int_{-a}^a x^4 p(x) dx = \left(\frac{1}{2a} \right) \frac{x^5}{5} \Big|_{-a}^a = \frac{a^4}{5}.$

19. Family probabilities.

Given that there are three children in your family, what is the probability that:

- (a) two are boys and one is a girl?
- (b) all three are girls?

The probability is about 1/2 for having either a boy or a girl. The binomial distribution shows that the probabilities are:

$$\begin{aligned} 3 \text{ girls} & \quad \left(\frac{1}{2} \right)^3 \frac{3!}{3!0!} = \frac{1}{8} \\ 2 \text{ girls, 1 boy} & \quad \left(\frac{1}{2} \right)^3 \frac{3!}{2!1!} = \frac{3}{8} \\ 1 \text{ girl, 2 boys} & \quad \left(\frac{1}{2} \right)^3 \frac{3!}{1!2!} = \frac{3}{8} \\ 3 \text{ boys} & \quad \left(\frac{1}{2} \right)^3 \frac{3!}{0!3!} = \frac{1}{8}. \end{aligned}$$

20. Evolutionary fitness.

Suppose that the probability of having the dominant allele (D) in a gene is p and the probability of the recessive allele (R) is $q = 1 - p$. You have two alleles, one from each parent.

- (a) Write the probabilities of all the possibilities: DD, DR, and RR.
- (b) If the fitness of DD is f_{DD} , the fitness of DR is f_{DR} , and the fitness of RR is f_{RR} , write the average fitness in terms of p .

		D	R	
				DD :
	D	p^2	pq	p^2
	R	qp	q^2	$2pq$
				RR :
				q^2

- (b) The average fitness is

$$\begin{aligned}
 \langle \text{fitness} \rangle &= \sum_i (\text{fitness})_i \text{probability}_i \\
 &= f_{DD}p^2 + 2f_{DR}p(1-p) + f_{RR}(1-p)^2.
 \end{aligned}$$

21. Ion-channel events.

A biological membrane contains N ion-channel proteins. The fraction of time that any one protein is open to allow ions to flow through is q . Express the probability $P(m, N)$ that m of the channels will be open at any given time.

Channels are either open, with probability q or closed, with probability $(1 - q)$, so the expression we want is the binomial distribution,

$$P(m, N) = q^m(1 - q)^{N-m} \frac{N!}{m!(N - m)!}.$$

22. Joint probabilities: balls in a barrel.

For Example 1.9, two green balls and one red ball drawn from a barrel without replacement:

- (a) Compute the probability $p(RG)$ of drawing one red and one green ball in either order.
- (b) Compute the probability $p(GG)$ of drawing two green balls.

(a) We have

$$\begin{aligned}p(G_1) &= 2/3, \\p(R_1) &= 1/3, \\p(G_2 | G_1) &= 1/2, \\p(G_2 | R_1) &= 1, \\p(R_2 | G_1) &= 1/2,\end{aligned}$$

so

$$\begin{aligned}p(RG) &= p(R_1)p(G_2 | R_1) + p(G_1)p(R_2 | G_1) \\&= (1/3)(1) + (2/3)(1/2) \\&= 2/3.\end{aligned}$$

$$\begin{aligned}\text{(b)} \quad p(GG) &= p(G_1)p(G_2 | G_1) \\&= (2/3)(1/2) = 1/3.\end{aligned}$$

Note that since $p(RR) = 0$, the quantities in (a) and (b) sum to one.

23. Sports and weather.

The San Francisco football team plays better in fair weather. They have a 70% chance of winning in good weather, but only a 20% chance of winning in bad weather.

- (a) If they play in the Super Bowl in Wisconsin and the weatherman predicts a 60% chance of snow that day, what is the probability that San Francisco will win?
- (b) Given that San Francisco lost, what is the probability that the weather was bad?

- (a) These chances of winning given in the problem are conditional probabilities (i.e., the probability of winning) given that the weather is good or bad. The approach here is to elucidate the four mutually exclusive and collectively exhaustive outcomes, winning and good weather, $P(W, G)$, winning and bad weather, $P(W, B)$, losing and good weather, $P(L, G)$, and losing and bad weather, $P(L, B)$. These joint probabilities can be related to the conditional probabilities, $P(W|G)$, etc., and the weather probabilities, $P(G)$ and $P(B)$ by the following equations:

$$P(W, G) = P(W|G)P(G) = (0.7)(0.4) = 0.28$$

$$P(W, B) = P(W|B)P(B) = (0.2)(0.6) = 0.12$$

$$P(L, G) = P(L|G)P(G) = (0.3)(0.4) = 0.12$$

$$P(L, B) = P(L|B)P(B) = (0.8)(0.6) = 0.48$$

(Note that $P(L|G)$ was computed from using the fact that $P(W|G) + P(L|G) = 1$.)

$$(b) \quad P(B|L) = \frac{P(L, B)}{P(L)}$$

$$\begin{aligned} P(L) &= P(L|G)P(G) + P(L|B)P(B) \\ &= (0.3)(0.4) + (0.8)(0.6) \\ &= 0.6 \end{aligned}$$

Therefore, $P(B|L) = 0.48/0.6 = 0.8$ —there is an 80% chance there was bad weather, given that they lost.

24. The Monty Hall Dilemma.

You are a contestant on a game show. There are three closed doors: one hides a car, and two hide goats. You point to one door, call it C . The gameshow host, knowing what's behind each door, now opens either door A or B , to show you a goat; say it's door A . To win a car, you now get to make your final choice: should you stick with your original choice C , or should you now switch and choose door B ? (*New York Times*, July 21, 1991; *Sci Amer*, August 1998.)

A good way to illustrate how people sometimes try to tackle this problem is to consider a similar one: Suppose three cards are lying face down on a table, only one of which is an ace. The first card is turned over, and is *not* an ace, so

$$p(B = \text{ace}) = \frac{\frac{1}{3}}{1 - \frac{1}{3}} = \frac{1}{2} \quad p(C = \text{ace}) = \frac{\frac{1}{3}}{1 - \frac{1}{3}} = \frac{1}{2}$$

So both remaining face-down cards are equally likely to be an ace. Using this type of reasoning, many people will say that switching isn't any more likely to win than staying with the door you initially chose. But these problems are not equivalent – in the Monty Hall case, the host has knowledge of both which door you initially picked and which door contains the car.

A simple way to come to arrive at the correct solution is to break it down into two separate questions:

1. What is the probability of winning if you *don't switch* doors?

If you *don't* switch doors, it means that you make no use of the information given by the host revealing a goat. The only way you can win is if the door you initially chose has the car behind it, and hence the probability of winning is $1/3$.

2. What is the probability of winning if you *do switch*?

If you *do* switch doors, the only way you can lose is if the door you initially picked had the car behind it, so you have a $1/3$ probability of losing and your probability of winning is therefore $2/3$. So you should switch doors.

25. Probabilities of picking cards and rolling dice.

- (a) What is the probability of drawing either a Queen or a Heart in a normal deck of 52 cards?
- (b) What is the probability P of getting three 2's and two 4's on 5 independent rolls of a die?

- (a) $P(\text{Q of Hearts}) = \frac{1}{52}$. $P(\text{Q not of Hearts}) = \frac{3}{52}$. $P(\text{Heart and not a Q}) = \frac{12}{52}$.
 $P = \frac{1}{52} + \frac{3}{52} + \frac{12}{52} = \frac{16}{52}$.
- (b) $P(2) = P(4) = \frac{1}{6}$. $P(2)^3 P(4)^2 = (\frac{1}{6})^5 = \frac{1}{7776} = 1.29 \cdot 10^{-4}$.
 $P = \binom{5}{2} 1.29 \cdot 10^{-4} = 1.29 \cdot 10^{-3}$.

26. Probability and translational start codons.

In prokaryotes, translation of mRNA messages into proteins is most often initiated at start codons on the bacterial mRNA having sequence "AUG." Assume that the mRNA is single-stranded and consists of a sequence of bases, each described by a single letter. The alphabet of letters for mRNA consists of "A", "C", "U", "G". Consider the set of all random pieces of bacterial mRNA of length six bases.

- (a) What is the probability of having either no A's OR no U's in the mRNA sequence of six base pairs long?
- (b) What is the probability of a random piece of mRNA having exactly 1 A, 1 U, and 1 G?
- (c) What is the probability of a random piece of mRNA of length six base pairs having an "A" directly followed by a "U" directly followed by a "G"; in other words, having an "AUG" in the sequence?
- (d) What is the total number of random pieces of mRNA of length six base pairs that have exactly one "A", exactly one "U", and exactly one "G", with "A" appearing first, then the "U", then the "G"? (ex: AXXUXG)

- (a) $P(\text{no A's OR no U's}) = P(\text{no A}) + P(\text{no U}) - P(\text{no A AND no U})$

$$= \left(\frac{3}{4}\right)^6 + \left(\frac{3}{4}\right)^6 - \left(\frac{1}{2}\right)^6$$

$$= 0.34$$

(b) Use the Multinomial Probability Distribution (eq. 1.31)

$$W = \frac{6!}{1!1!1!3!}, P = \left(\frac{1}{4}\right)^6 \cdot \frac{6!}{1!1!1!3!} = 0.0293$$

(c) Let us find $W(\text{AUG})$:

6 positions total:

3 positions are fixed: $W_f = 1^3$

3 positions are variable: $W_v = 4^3$

4 positions "AUG" can take in the sequence: $W_{pos} = 3$

A U G _ _ _
_ A U G _ _
_ _ A U G _

Note: We do not count this next "AUG" position because it has already been included in the first A U G _ _ _ when we count the multiplicity of the variable positions:

_ _ _ A U G

Because W_{total} is the product of independent sources of multiplicity,

$$W(\text{AUG}) = W_f \cdot W_v \cdot W_{pos} = 1^3 \cdot 4^3 \cdot 3$$

$$P(\text{AUG}) = \frac{W_f}{W_{total}} = \frac{3 \cdot 4^3}{4^6} = \frac{3}{4^3} = \frac{3}{64} \approx 0.0469$$

(d) We will calculate W for 1A, 1U, and 1G for any ordering of the A, U, G with respect to each other. Then we will divide this result by the number of ways of ordering A, U, G with respect to each other, because we wish only to count the cases where A appears before U appears before G.

$$W(1A, 1U, 1G) = \frac{6!}{1!1!1!3!}$$

The number of ways of ordering A, U, G with respect to each other : $3!$

$$W(1A, 1U, 1G) = \frac{\frac{6!}{1!1!1!3!}}{3!} = \frac{6 \cdot 5 \cdot 4}{3 \cdot 2 \cdot 1} = 20$$

27. DNA synthesis.

Suppose you synthesize a strand of DNA that is 1000 bases long. A process you use introduces a wrong base on average every 1000 bases synthesized.

- Calculate and draw a bar graph indicating the yield (probability) of each product DNA, containing 0, 1, 2 and 3 mutations.
- Calculate how many combinations of DNA sequences of 1000 bases long contain exactly 2 mutant bases.
- What is the probability of having the 500th base and the 888th base mutated in the pool of DNA which has only two mutations?
- What is the probability of having two mutations side-by-side in the pool of DNA which has only two mutations?

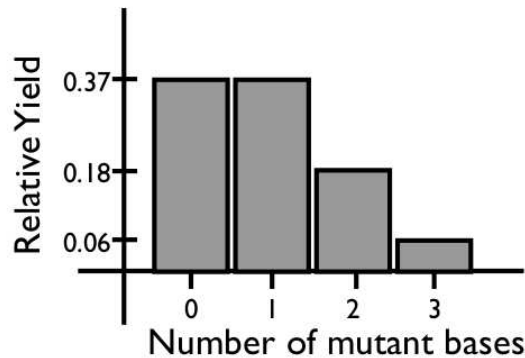
- Let letter R stand for a right base, and M stand for a mutant one.

$$p(1000R, 1000) = (0.999)^{1000} (0.001)^0 \frac{1000!}{1000!} \approx 0.368$$

$$p(999R, 1M, 1000) = (0.999)^{999} (0.001)^1 \frac{1000!}{999!1!} \approx 0.368$$

$$p(998R, 2M, 1000) = (0.999)^{998} (0.001)^2 \frac{1000!}{998!2!} \approx 0.18$$

$$p(997R, 2M, 1000) = (0.999)^{997} (0.001)^3 \frac{1000!}{997!3!} \approx 0.06$$



$$(b) W = \frac{1000!}{998!2!}$$

- The probability of having a DNA strand with only 2 mutated bases is 0.18. The probability of having mutations at places 500 and 888 of the strand is

$$p(\dots M(500) \dots M(888) \dots) = 0.18 \cdot \frac{998!2!}{1000!} = 0.18 \cdot 2 \cdot 10^{-6} = 3.6 \cdot 10^{-7}$$

$$(d) p(\dots MM \dots) = 0.18 \cdot \frac{998!2!}{1000!} \cdot 999 = 0.18 \cdot \frac{1}{500} = 3.6 \cdot 10^{-4}$$

28. Presidential election.

Two candidates are running for President. Candidate A has already received 80 electoral votes and only needs 35 more to win. Candidate B already has 50 votes, and needs 65 more to win.

Five states remain to be counted. Winning a state gives a candidate 20 votes; losing gives the candidate zero votes. Assume both candidates otherwise have equal chances to win in those 5 states:

- (a) Write an expression for $W_{A, \text{total}}$, the number of ways A can succeed at winning 40 more electoral votes.
- (b) Write the corresponding expression for $W_{B, \text{total}}$.
- (c) What is the probability candidate A beats candidate B?

(a) For candidate A, this is like flipping a coin 5 times. Each head is like winning 20 points; each tail is zero. Candidate A can win by getting 2 or more states ('heads'), so:

$$W_{A, \text{total}} = \frac{5!}{2!3!} + \frac{5!}{3!2!} + \frac{5!}{4!1!} + \frac{5!}{5!0!} = 10 + 10 + 5 + 1 = 26.$$

(b) Candidate B can win by getting 3 or more states, so:

$$W_{B, \text{total}} = \frac{5!}{4!1!} + \frac{5!}{5!0!} = 5 + 1 = 6.$$

(c)

$$P(\text{A wins}) = \frac{W_{A, \text{total}}}{W_{A, \text{total}} + W_{B, \text{total}}} = \frac{26}{26 + 6} = 0.81.$$

Chapter 2

Extremum Principles Predict Equilibria

1. A lattice gas.

How many arrangements are there of fifteen indistinguishable lattice gas particles distributed on:

- (a) $V = 20$ sites?
- (b) $V = 16$ sites?
- (c) $V = 15$ sites?

$$(a) \quad W(N = 15, V = 20) = \frac{20!}{15!5!} = \frac{20 \cdot 19 \cdot 18 \cdot 17 \cdot 16}{5 \cdot 4 \cdot 3 \cdot 2} = 15,504$$

$$(b) \quad W(N = 15, V = 16) = \frac{16!}{15!1!} = 16$$

$$(c) \quad W(N = 15, V = 15) = \frac{15!}{15!0!} = 1$$

2. Maximum of binomial distribution.

Find the value $n = n^*$ that causes the function

$$W = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}$$

to be at a maximum, for constants p and N . Use Stirling's approximation, $x! \simeq (x/e)^x$. Note that it is easier to find the value of n that maximizes $\ln W$ than the value that maximizes W . The value of n^* will be the same.

W is maximal where $\ln W$ is maximal, and

$$\ln W = n \ln p + (N-n) \ln(1-p) + \ln N! - \ln n! - \ln(N-n)!$$

Now using Stirling's approximation, $\ln N! \approx N \ln N - N$, we obtain

$$\begin{aligned} \ln W &\approx n \ln p + (N-n) \ln(1-p) + (N \ln N - N) - (n \ln n - n) \\ &\quad - [(N-n) \ln(N-n) - (N-n)] \\ &= n \ln p + (N-n) \ln(1-p) + N \ln N - n \ln n - (N-n) \ln(N-n) \end{aligned}$$

This function is maximal where

$$\begin{aligned} \frac{d \ln W}{dn} &= 0 \\ \frac{d \ln W}{dn} &= \ln p - \ln(1-p) - \left(n \cdot \frac{1}{n} + \ln n \right) \\ &\quad - \left((N-n) \cdot \frac{1}{(N-n)} + \ln(N-n) \cdot (-1) \right) \\ &= \ln \left(\frac{p}{1-p} \right) - \ln(n) + \ln(N-n) - 1 + 1 \end{aligned}$$

We add $\ln N - \ln N$ to the right-hand side and rearrange terms to allow us to write $\ln(n/N)$

and $\ln(N - n)/N$:

$$\begin{aligned}\frac{d \ln W}{dn} &= \ln\left(\frac{p}{1-p}\right) - \ln\left(\frac{n}{N}\right) + \ln\left(\frac{N-n}{N}\right) = 0 \\ \ln\left(\frac{n^*}{N-n^*}\right) &= \ln\left(\frac{p}{1-p}\right) \\ \frac{N^*}{N-n^*} &= \frac{p}{1-p} \\ n^* \left(1 + \frac{p}{1-p}\right) &= \frac{Np}{1-p} \\ \frac{n^*}{N} &= \frac{p/(1-p)}{1/1-p} = p.\end{aligned}$$

3. Finding extrema.

$$V(x) = \frac{x^3}{3} + \frac{5x^2}{2} - 24x :$$

(a) Where is the maximum?

(b) Where is the minimum?

To find the extrema, determine the values $x = x^*$ that cause the derivative to equal zero

$$\begin{aligned}\left. \frac{dV}{dx} \right|_{x^*} &= (x^2 + 5x - 24) \Big|_{x^*} = (x^* - 3)(x^* + 8) = 0 \\ \implies x^* &= 3, -8.\end{aligned}$$

To determine whether the extrema are maxima or minima, evaluate the second derivative at the x^* points

$$\frac{d^2V}{dx^2} = 2x + 5$$

$$\left. \frac{d^2V}{dx^2} \right|_{x^*=3} = 2(3) + 5 = 11.$$

Since this value is positive, $x^* = 3$ is a minimum.

$$\left. \frac{d^2V}{dx^2} \right|_{x^*=-8} = 2(-8) + 5 = -9.$$

This value is negative, so $x^* = -8$ is a maximum.

4. The binomial distribution narrows as N increases.

Flip a coin $4N$ times. The most probable number of heads is $2N$, and its probability is $p(2N)$. If the probability of observing N heads is $p(N)$, show that the ratio $p(N)/p(2N)$ diminishes as N increases.

$$\begin{aligned} \frac{p(N)}{p(2N)} &= \frac{\left(\frac{(4N)!}{(N!)(3N)!} \right)}{\left(\frac{(4N)!}{(2N)!(2N)!} \right)} \\ &= \frac{[(2N)!]^2}{N!(3N)!} \approx \frac{\left[\left(\frac{2N}{e} \right)^{2N} \right]^2}{\left(\frac{N}{e} \right)^N \left(\frac{3N}{e} \right)^{3N}} \\ &= \frac{2^{4N} N^{4N}}{3^{3N} N^{4N}} \\ &= \left(\frac{2^4}{3^3} \right)^N = \left(\frac{16}{27} \right)^N \end{aligned}$$

Note that as $N \rightarrow \infty$

$$\lim_{N \rightarrow \infty} \frac{p(N)}{p(2N)} = \lim_{N \rightarrow \infty} \left(\frac{16}{27} \right)^N = 0$$

5. De-mixing is improbable.

Using the diffusion model of Example 2.3, with $2V$ lattice sites on each side of a permeable wall and a total of $2V$ white particles and $2V$ black particles, show that perfect de-mixing (all white on one side, all black on the other) becomes increasingly improbable as V increases.

The ratio r of the perfectly demixed to perfectly mixed configurations is

$$r = \frac{1}{\binom{2V!}{V!V!}} = \left(\frac{V!V!}{(2V)!} \right)^2 \approx \left(\frac{\left(\frac{V}{e}\right)^{2V}}{\left(\frac{2V}{e}\right)^{2V}} \right)^2 = \left(\frac{1}{2^4} \right)^V = \left(\frac{1}{16} \right)^V$$

Note that as $V \rightarrow \infty$

$$\lim_{r \rightarrow \infty} r = \lim_{N \rightarrow \infty} \left(\frac{1}{16} \right)^N = 0$$

6. Stable states.

For the energy function $V(\theta) = \cos \theta$ for $0 \leq \theta \leq 2\pi$, find the values $\theta = \theta_s$ that identify stable equilibria, and the values $\theta = \theta_u$ that identify unstable equilibria.

$$\frac{dV(\theta)}{d\theta} = -\sin \theta.$$

This derivative is zero when $\sin \theta$ is zero. This occurs at $\theta = n\pi$, where n is an integer. To determine which of these points are maxima and which are minima, we need to compute the second derivative.

$$\frac{d^2V}{d\theta^2} = -\cos \theta$$

This is negative for all even-numbered multiples of π and positive for all odd-numbered multiples. Therefore, the unstable equilibria are given by $\theta_u = 2k\pi$ and the stable equilibria by $\theta_s = \pi + 2k\pi$, where k is an integer.

7. One dimensional lattice.

You have a 1-dimensional lattice that contains N_A particles of type A and N_B particles of type B . They completely fill the lattice, so the number of sites is $N_A + N_B$. Write an expression for the multiplicity $W(N_A, N_B)$, the number of distinguishable arrangements of the particles on the lattice.

$$W(N_A, N_B) = \binom{N_A + N_B}{N_A} = \binom{N_A + N_B}{N_B} = \frac{(N_A + N_B)!}{N_A! N_B!}$$

Chapter 3

Heat, Work and Energy

1. The time dependence of a mass on a spring.

- (a) For the harmonic motion of a mass on a spring, the kinetic energy is $K = (1/2)mv^2$, and the potential energy is $V = (1/2)k_s x^2$, where k_s is the spring constant. Using the conservation of energy find the time-dependent spring displacement, $x(t)$.
- (b) Compute the force $f(t)$ on the mass.

Harmonic motion is the model for a bond stretching in molecules and for the motions of atoms in crystals around their equilibrium positions. Harmonic motion can be pictured as a spring motion. The potential energy of a spring is given by $V(x) = (1/2)k_s x^2$, where k is a constant that depends on the characteristics of the spring. Writing the equation for conservation of energy, we have

$$\frac{m\dot{x}(t)^2}{2} + \frac{k_s x(t)^2}{2} = E.$$

Here, $\dot{x}(t) = \frac{dx(t)}{dt}$. Rearranging terms, we get

$$\dot{x}(t)^2 = \frac{2E}{m} - \frac{k_s}{m}x(t)^2$$

To simplify things, we introduce a constant $\omega^2 = k_s/m$

$$\dot{x}(t)^2 = \omega^2 \left(\frac{2E}{m\omega^2} - x(t)^2 \right) = \omega^2 \left(\frac{2E}{k_s} - x(t)^2 \right)$$

Introducing another constant $A = \frac{2E}{k_s}$, we arrive at

$$\dot{x}(t)^2 = \omega^2 (A^2 - x(t)^2)$$

We can integrate this with another trick that is sometimes possible to use on simple differential equations:

$$\begin{aligned} \left(\frac{dx}{dt} \right)^2 &= \omega^2 (A^2 - x^2) \\ \frac{dx}{dt} &= \omega (A^2 - x^2)^{1/2} \\ \frac{dx}{(A^2 - x^2)^{1/2}} &= \omega dt \\ \int_0^x \frac{dx'}{(A^2 - x'^2)^{1/2}} &= \int_0^t \omega dt' \end{aligned}$$

The integral on the left is an inverse trigonometric integral, and the integral on the right is trivial.

$$\omega t + \phi = \sin^{-1} \left(\frac{x}{A} \right)$$

Therefore, the equation of motion is

$$x(t) = A \sin(\omega t + \phi)$$

The force on the particle as a function of time can be determined from the spatial derivative of the potential

$$f(t) = - \left. \frac{dV}{dx} \right|_{x(t)} = -k_s x(t) = -k_s A \sin(\omega t + \phi)$$

or from the time derivative of the position

$$\begin{aligned}
 f(t) &= m\ddot{x}(t) \\
 &= m\frac{d\dot{x}(t)}{dt} \\
 &= -mA\omega^2 \sin(\omega t + \phi) \\
 &= -k_s A \sin(\omega t + \phi)
 \end{aligned}$$

2. Equalizing energies.

For the two 10-particle two-state systems of Example 3.4, suppose the total energy to be shared between the two objects is $U = U_A + U_B = 4$. What is the distribution of energies that gives the highest multiplicity?

We can write

$$W(U_A) = \left(\frac{10!}{U_A!(10 - U_A)!} \right) \left(\frac{10!}{(4 - U_A)!(10 - 4 + U_A)!} \right).$$

The following table lists all the possibilities

U	$W(U)$
0	210
1	1200
2	2025
3	1200
4	210

This shows that the highest multiplicity occurs, in this case, when the energy is divided equally between the two objects.

3. Energy conversion.

When you drink a beer, you get about 100 cal (1 food cal = 1 kcal). You can work this off on an exercise bicycle in about 10 minutes. If you hook your exercise bicycle to a generator, what wattage of light bulb could you light up, assuming 100% efficiency?

$$(100 \text{ cal}) \left(4.18 \frac{\text{J}}{\text{cal}} \right) \left(\frac{1}{10 \text{ min}} \right) \left(\frac{1 \text{ min}}{60 \text{ sec}} \right) = 697 \frac{\text{J}}{\text{sec}} = 697.6 \text{ watts.}$$

An interesting comparison is that 1 horsepower = 746 watts.

4. Kinetic energy of a car.

How much kinetic energy does a 1700 kg car have, if it travels 100 km h⁻¹?

$$\begin{aligned} \text{Kinetic energy} &= \frac{1}{2}mv^2 \\ &= \left(\frac{1}{2} \right) (1700 \text{ kg}) \left[\left(\frac{10^5 \text{ meters}}{\text{hr}} \right) \left(\frac{1 \text{ hr}}{3600 \text{ sec}} \right) \right]^2 \\ &= 655.8 \text{ kJ} \end{aligned}$$

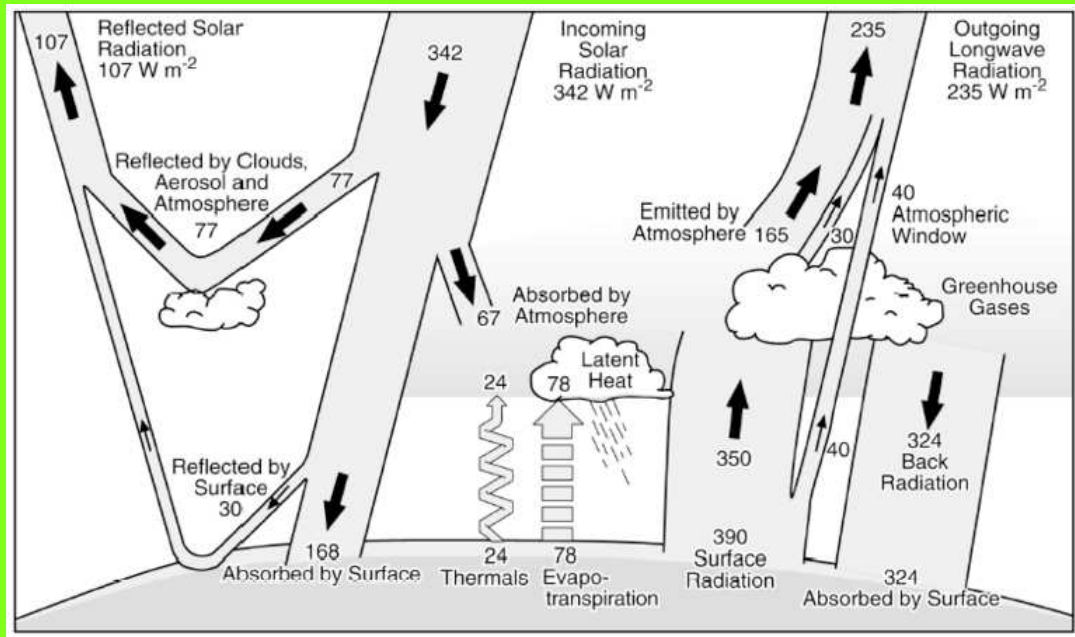
5. Rms velocity of a gas.

Using $\frac{1}{2}kT = \frac{1}{2}m\langle v_x^2 \rangle$, for T = 300 K, compute the rms velocity, $\langle v_x^2 \rangle^{\frac{1}{2}}$, of O₂ gas.

$$\begin{aligned} \langle v_x^2 \rangle &= \frac{kT}{M} \\ M &= 32 \frac{\text{g}}{\text{mol}} \cdot \frac{1 \text{ mol}}{6.02 \cdot 10^{23} \text{ molecules}} \cdot \frac{\text{kg}}{1000 \text{ g}} = 5.316 \cdot 10^{-26} \frac{\text{kg}}{\text{molecule}} \\ \langle v_x^2 \rangle &= 1.381 \cdot 10^{-23} \frac{\text{J}}{\text{K}} \cdot 300 \text{ K} \cdot \frac{1}{5.316 \cdot 10^{-26}} \frac{\text{molecules}}{\text{kg}} = 77,934.5 \frac{\text{m}^2}{\text{s}^2} \\ (1 \text{ J} &= 1 \text{ kg} \frac{\text{m}^2}{\text{s}^2}) \\ \langle v_x^2 \rangle^{\frac{1}{2}} &= 279.2 \frac{\text{m}}{\text{s}} \end{aligned}$$

6. Earth's energy balance

The figure below shows energy inputs and outputs to the earth, in Watts/m², which is a measure of energy per unit area per unit time (1 W = 1 V · 1 A).



- Suppose your backyard has an area of 1000 m². Your yard only receives sunlight about one third of each day, and because of overcast skies, let's say the total flux is reduced by another factor of one half. What average energy flux, in Watts/m², does your yard receive?
- Your cell phone uses about 2 W. Assuming 20% efficiency, how big a solar cell would you need to power it?
- If we had no *natural* greenhouse gases (CO₂ and water vapor), how would that shift earth's energy balance?
- How much energy, in Watt-hours, is in a gallon of gasoline? Assume that 100% of the gasoline is octane (C₈H₁₈). Gasoline is about 1 g/cc, and each carbon-carbon covalent bond is worth about 60 kcal/mol. Assume 50% efficiency in burning.

- Energy flux absorbed by every m² of earth: $168 + 324 \approx 500 \frac{W}{m^2}$
 Energy flux absorbed by the backyard: $(500 \frac{W}{m^2} \cdot 1000 m^2) \cdot (\frac{1}{3}) \cdot (\frac{1}{2}) \approx 83333 W$
- The amount of power a solar cell can convert per m² is $\approx \frac{16667 W}{1000 m^2} = 16.67 \frac{W}{m^2}$
 For 2 watts, one would need a $\frac{2}{16.67} \approx 0.12 m^2$ solar cell

- (c) The earth would lose $\frac{324}{324+168} \approx 66\%$ of the radiation absorbed at the surface. Essentially, the earth would cool down significantly.
- (d) 100% octane, gasoline ~ 1 g/ml, a C-C bond $\sim 60 \frac{kcal}{mol} = 2.51 \cdot 10^5 \frac{J}{mol}$, 50% efficiency
 $C_8H_{18} = 114 \frac{g}{mol}$, 7 C-C bonds in one octane molecule
 $1gallon \cdot \frac{3.785L}{1gallon} \cdot \frac{1kg}{1L} = 3.785kg$ of octane.
 $3785g \text{ octane} \cdot \frac{mol_{octane}}{114g} \cdot \frac{7mol_{C-Cbonds}}{1mol_{octane}} \cdot \frac{251000J}{mol_{C-Cbonds}} = 5.83 \cdot 10^7 J$
 At 50% efficiency, we have $2.92 \cdot 10^7 J = 2.92 \cdot 10^7 W \cdot s = 8102 W \cdot hr$

7. Taking the earth's temperature

A physical law, called the Stefan-Boltzmann (SB) law, relates the transfer rate of electromagnetic radiation of a body (called *black-body radiation*) to its temperature. The SB law is a relative of the *Wein law*, the principle that explains why an object that is hot enough will emit visible light, as when a burning ember in a fire glows red, or glows blue if it is even hotter. An object having a non-zero temperature will emit electromagnetic radiation. Conversely, an object that absorbs energy *via* radiation, increases its temperature. The SB law says that the electromagnetic power P is related to the temperature T by

$$P = (5.67 \times 10^{-8} \frac{W}{m^2 K^4}) T^4 \quad (1)$$

- (a) If the incoming solar power hitting the earth is $P = 342 \text{ Wm}^{-2}$, what would you predict should be the earth's temperature?
- (b) Now, turn around this argument around. The earth's actual average temperature is $T = 288K$ or $+15^\circ \text{ C}$. Use the SB law to compute the power of radiated heat from the earth's core.

- (a) Using the SB law, the earth's estimated temperature would be $T = 255K$, or -18° C .
- (b) Using the SB law, the power radiated from the earth's core would be $P = 390 \text{ Wm}^{-2}$.

8. Why do elephants live longer than mice?

Let L represent the lifespan of an organism. It is known that all mammalian species live, on average, to have about 1.5×10^9 heartbeats (HB), independent of their size. Assume that an organism will have a total of $HB = L \times HR = \text{constant heartbeats during its lifetime}$, where HR is its heart-rate. What assumptions would you need to make to explain the observation that the lifespans of organisms grow with body mass M as $L \propto \frac{HB}{HR} \propto M^{1/4}$?

Assume the rate of energy expenditure per unit mass (BMR/M) of biological tissue is proportional to energy flow into that tissue. This energy flow is proportional to the rate of blood flow. And, assume that blood flow correlates with the heart rate (HR) of an organism. Then, you have $HR \propto BMR/M \propto M^{-1/4}$, indicating that heart rates decrease in larger organisms, consistent with observations. Combining these observations gives

$$L \propto \frac{HB}{HR} \propto M^{1/4}, \tag{2}$$

rationalizing why elephants live longer than mice. This, too, is one of the 1/4-power scaling laws observed in nature.

Chapter 4

Math Tools: Multivariate Calculus

1. Applying the Euler test.

Which of the following are exact differentials?

- (a) $6x^5dx + dy$
- (b) $x^2y^2dx + 3x^2y^3dy$
- (c) $(1/y)dx - (x/y^2)dy$
- (d) $ydx + 2xdy$
- (e) $\cos xdx - \sin ydy$
- (f) $(x^2 + y)dx + (x + y^2)dy$
- (g) $x dx + \sin y dy$

If you have an exact differential, then $dg(x, y) = u(x, y)dx + v(x, y)dy$.

	$\frac{\partial u}{\partial y}$	$\frac{\partial v}{\partial x}$		$g(x,y)$
(a)	0	0	exact	$x^6 + y$
(b)	$2x^2y$	$6xy^3$	inexact	
(c)	$-y^{-2}$	$-y^{-2}$	exact	xy^{-1}
(d)	1	2	inexact	
(e)	0	0	exact	$\sin x + \cos y$
(f)	1	1	exact	$\frac{x^3}{3} + \frac{y^3}{3} + xy$
(g)	0	0	exact	$\frac{x^2}{2} - \cos y$

2. Differentiating multivariate functions.

Compute the partial derivatives, $(\partial f / \partial x)_y$ and $(\partial f / \partial y)_x$, for the following functions.

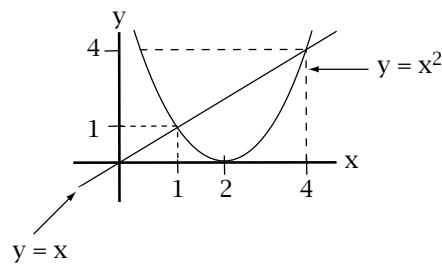
- (a) $f(x, y) = 3x^2 + y^5$
- (b) $f(x, y) = x^{10}y^{1/2}$
- (c) $f(x, y) = x + y^2 + 3$
- (d) $f(x, y) = 5x$

- (a) $\left(\frac{\partial f}{\partial x}\right)_y = 6x \quad \left(\frac{\partial f}{\partial y}\right)_x = 5y^4$
- (b) $\left(\frac{\partial f}{\partial x}\right)_y = 10x^9y^{1/2} \quad \left(\frac{\partial f}{\partial y}\right)_x = \frac{1}{2}x^{10}y^{-1/2}$
- (c) $\left(\frac{\partial f}{\partial x}\right)_y = 1 \quad \left(\frac{\partial f}{\partial y}\right)_x = 2y$
- (d) $\left(\frac{\partial f}{\partial x}\right)_y = 5 \quad \left(\frac{\partial f}{\partial y}\right)_x = 0$

3. Minimizing a single variable function subject to a constraint.

Given the function $y = (x - 2)^2$, find x^* , the value of x that minimizes y subject to the constraint $y = x$.

You do not need anything sophisticated like Lagrange multipliers for this problem because you have two equations in two unknowns. It can be solved directly. Lagrange multipliers are needed only when you have more unknowns than equations.



$$\begin{aligned}\text{Substitute } y &= x \text{ into } y = (x - 2)^2 \\ y &= (y - 2)^2 = y^2 - 4y + 4 \\ \text{or } y^2 - 5y + 4 &= 0 \\ (y - 1)(y - 4) = 0 &\implies y = 1 \text{ or } 4\end{aligned}$$

The two solutions are

$$(x, y) = (1, 1) \text{ or } (4, 4)$$

The lowest of these is $(x, y) = (1, 1)$.

4. Maximizing a multivariate function without constraints.

Find the maximum (x^*, y^*, z^*) of the function $f(x, y, z) = d - (x - a)^2 - (y - b)^2 - (z - c)^2$.

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = 0 \quad -2(x^* - a) = 0 \implies x^* = a$$

$$\left(\frac{\partial f}{\partial y}\right)_{x,z} = 0 \quad -2(y^* - b) = 0 \implies y^* = b$$

$$\left(\frac{\partial f}{\partial z}\right)_{x,y} = 0 \quad -2(z^* - c) = 0 \implies z^* = c$$

The extremum is $(x^*, y^*, z^*) = (a, b, c)$ and the maximum value is $f(a, b, c) = d$.

5. Extrema of multivariate functions with constraints.

- (a) Find the maximum of the function $f(x, y) = -(x - a)^2 - (y - b)^2$ subject to the constraint $y = kx$.
- (b) Find the minimum of the paraboloid $f(x, y) = (x - x_0)^2 + (y - y_0)^2$ subject to the constraint $y = 2x$.

(a) Use the Lagrange multiplier method. Let $g(x, y) = y - kx$. We want

$$\left(\frac{\partial f}{\partial x}\right) - \lambda \left(\frac{\partial g}{\partial x}\right) = 0 \tag{3}$$

and

$$\left(\frac{\partial f}{\partial y}\right) - \lambda \left(\frac{\partial g}{\partial y}\right) = 0 \tag{4}$$

$$-2(x^* - a) - \lambda(-k) = 0 \tag{5}$$

$$-2(y^* - b) - \lambda = 0 \tag{6}$$

Substituting $y = kx$ into Equation (6) gives:

$$-2(kx^* - b) = \lambda$$

Substituting this expression for λ into Equation (5) gives

$$x^* = \frac{a + kb}{1 + k^2} \quad y^* = \frac{k(a + kb)}{1 + k^2}$$

(b) $g(x, y) = y - 2x$

$$2(x^* - x_0) + 2\lambda = 0$$

$$2(y^* - y_0) - \lambda = 0$$

$$x^* - x_0 = -\lambda = -2(y^* - y_0).$$

Combined with the constraint $y^* = 2x^*$, this gives

$$x^* = \frac{x_0 + 2y_0}{5} \quad y^* = \frac{2}{5}(x_0 + 2y_0)$$

6. Composite functions.

(a) Given the functions $f(x, y(u)) = x^2 + 3y^2$ and $y(u) = 5u + 3$, express df in terms of changes dx and du .

(b) What is $\left(\frac{\partial f}{\partial u}\right)_{x,u=1}$?

$$\begin{aligned} \text{(a)} \quad df &= \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) \left(\frac{dy}{du}\right) du \\ df &= 2x dx + (6y)(5) du \\ &= 2x dx + 30y du = 2x dx + 30(5u + 3) du \end{aligned}$$

$$\text{(b)} \quad \left(\frac{\partial f}{\partial u}\right) = \left(\frac{\partial f}{\partial y}\right) \left(\frac{dy}{du}\right) = 30(5u + 3)|_{u=1} = 240.$$

7. Converting to an exact differential.

Given the expression $dx + (x/y)dy$, show that dividing by x results in an exact differential. What is the function $f(x, y)$ such that df is $dx + (x/y)dy$ divided by x ?

Dividing $dx + (x/y)dy$ by x gives $(dx/x) + (dy/y)$. Euler's test

$$\left(\frac{\partial(1/x)}{\partial y}\right) = 0 = \left(\frac{\partial(1/y)}{\partial x}\right) = 0.$$

Thus $(dx/x) + (dy/y)$ is path independent, and can be integrated to give $\int(dx/x) + (dy/y) = \ln(xy) + \text{constant} = f(x, y)$.

8. Propagation of error.

Suppose that you can measure independent variables x and y and that you have a dependent variable $f(x, y)$. The average values are \bar{x} , \bar{y} , and \bar{f} . We define the *error* in x as the deviations $\varepsilon_x = x - \bar{x}$, in y as $\varepsilon_y = y - \bar{y}$, and in f as $\varepsilon_f = f - \bar{f}$.

- (a) Use a Taylor series expansion to express the error, ε_f , in f , as a function of the errors ε_x and ε_y in x and y .
- (b) Compute the mean-squared error $\langle \varepsilon_f^2 \rangle$ as a function of $\langle \varepsilon_x^2 \rangle$ and $\langle \varepsilon_y^2 \rangle$.
- (c) Consider the ideal gas law with $f = p$, $x = T$, and $y = V$. If T and V have 10% random errors, how big will be the error in p ?
- (d) How much increase in $\varepsilon(f)$ comes from adding n measurements that all have the same uncorrelated error $\varepsilon(x)$?

- (a) To find the error in f if you know the error in x , use a Taylor series expansion about \bar{x} :

$$\begin{aligned} f(x) - \bar{f} &= \left. \frac{df}{dx} \right|_{\bar{x}} (x - \bar{x}) + \frac{1}{2} \left. \frac{d^2f}{dx^2} \right|_{\bar{x}} (x - \bar{x})^2 + \dots \\ \implies \varepsilon_f &= \left. \frac{df}{dx} \right|_{\bar{x}} \varepsilon_x + \frac{1}{2} \left. \frac{d^2f}{dx^2} \right|_{\bar{x}} \varepsilon_x^2 + \dots \end{aligned}$$

If the error in x is small, $\varepsilon_x \ll 1$ and we can neglect terms that are second-order or

higher in ε_x :

$$\varepsilon_f \approx \left. \frac{df}{dx} \right|_{\bar{x}} \varepsilon_x$$

(b) Generalizing this to errors in x and y gives

$$\varepsilon_f = \left(\frac{\partial f}{\partial x} \right)_y \varepsilon_x + \left(\frac{\partial f}{\partial y} \right)_x \varepsilon_y$$

We are usually less interested in a single error and more interested in the average of the square of all the errors in a set of measurements, $\langle \varepsilon_f^2 \rangle$. (The average error itself, $\langle \varepsilon_f \rangle$, is less informative than $\langle \varepsilon_f^2 \rangle$ because positive and negative errors cancel resulting in $\langle \varepsilon_f \rangle \approx 0$. $\langle \varepsilon_f^2 \rangle$ is more useful because it tells us about the magnitudes of the errors.)

To get $\langle \varepsilon_f^2 \rangle$, we first square ε_f :

$$\begin{aligned} \varepsilon^2(f) &= \left[\left(\frac{\partial f}{\partial x} \right) \varepsilon_x + \left(\frac{\partial f}{\partial y} \right) \varepsilon_y \right]^2 \\ &= \left(\frac{\partial f}{\partial x} \right)^2 \varepsilon_x^2 + \left(\frac{\partial f}{\partial y} \right)^2 \varepsilon_y^2 + \left(\frac{\partial f}{\partial x} \right) \left(\frac{\partial f}{\partial y} \right) \varepsilon_x \varepsilon_y \end{aligned}$$

Now, we take the expectation value. We use the fact that x and y are independent, so their errors will be uncorrelated and $\langle \varepsilon_x \varepsilon_y \rangle = 0$:

$$\langle \varepsilon_f^2 \rangle = \left(\frac{\partial f}{\partial x} \right)^2 \langle \varepsilon_x^2 \rangle + \left(\frac{\partial f}{\partial y} \right)^2 \langle \varepsilon_y^2 \rangle.$$

(c) For one mole of an ideal gas

$$\left(\frac{\partial f}{\partial x} \right) = \left(\frac{\partial p}{\partial T} \right) = \frac{R}{V} \quad \text{and} \quad \left(\frac{\partial f}{\partial y} \right) = \left(\frac{\partial p}{\partial V} \right) = -\frac{RT}{V^2}.$$

We assume errors of 10%, so $\varepsilon_T/T = 0.1$ and $\varepsilon_V/V = 0.1$. Hence

$$\varepsilon_p^2 = \left(\frac{R}{V} \right)^2 T^2 (0.10)^2 + \left(\frac{RT}{V^2} \right)^2 V^2 (0.10)^2 = 2 \left(\frac{RT}{V} \right)^2 0.01 = 0.02 p^2$$

(d) n measurements gives $\varepsilon_f^2 = n \left(\frac{\partial f}{\partial x} \right)^2 \varepsilon_x^2$ so ε_f grows as $(\sqrt{n})\varepsilon_x$.

9. Small differences of large numbers can lead to nonsense.

Using the results from Problem 8, show that the propagated error is larger than the difference itself, for $f(x, y) = x - y$, with $x = 20 \pm 2$ and $y = 19 \pm 2$.

Since $(\partial f / \partial x)^2 = 1$ and $(\partial f / \partial y)^2 = 1$, we have $\varepsilon_f^2 = \varepsilon_x^2 + \varepsilon_y^2 = 8$. Since $\varepsilon_x = \varepsilon_y = z$ so $\varepsilon_f = \sqrt{8} = 2.83$. Therefore $(20 \pm 2) - (19 \pm 2) = 1 \pm 2.83$.

10. Finding extrema.

Find the point (x^*, y^*, z^*) that is at the minimum of the function

$$f(x, y, z) = 2x^2 + 8y^2 + z^2$$

subject to the constraint equation

$$g(x, y, z) = 6x + 4y + 4z - 72 = 0.$$

Use the Lagrange multiplier method:

$$\left(\frac{\partial f}{\partial x} \right) - \lambda \left(\frac{\partial g}{\partial x} \right) = 0$$

$$\left(\frac{\partial f}{\partial y} \right) - \lambda \left(\frac{\partial g}{\partial y} \right) = 0$$

$$\left(\frac{\partial f}{\partial z} \right) - \lambda \left(\frac{\partial g}{\partial z} \right) = 0$$

$$(4x) - \lambda(6) = 0$$

$$(16y) - \lambda(4) = 0$$

$$(2z) - \lambda(4) = 0$$

$$\lambda = \frac{2x}{3}$$

$$\lambda = 4y$$

$$\lambda = \frac{z}{2}$$

$$g(x, y, z) = 6x + 4y + 4z - 72 = 0$$

Find x:

$$\begin{aligned} 0 &= 6x + 4y + 4z - 72 \\ &= 6x + 4\left(\frac{2x}{12}\right) + 4\left(\frac{4x}{3}\right) - 72 \\ &= \left(\frac{36x}{3}\right) - 72 \\ x^* &= 6 \end{aligned}$$

Find y:

$$\begin{aligned} 0 &= 6x + 4y + 4z - 72 \\ &= 6(6) + 4y + 4(8y) - 72 \\ &= -36 + 36y \\ y^* &= 1 \end{aligned}$$

Find z:

$$\begin{aligned} 0 &= 6x + 4y + 4z - 72 \\ &= 6(6) + 4(1) + 4z - 72 \\ &= -32 + 4z \\ z^* &= 8 \end{aligned}$$

11. Derivative of a multivariable composite function.

For the function $f(x, y(v)) = x^2y + y^3$, where $y = mv^2$, compute $\frac{df}{dv}$ around the point where $m=1$, $v=2$, $x=3$.

$$\frac{dF}{dv} = \frac{\partial F}{\partial y} \cdot \frac{\partial y}{\partial v}$$

$$\frac{\partial F}{\partial y} = x^2 + 3y^2, \frac{\partial y}{\partial v} = 2mv$$

$$\frac{dF}{dv} = 2mv(x^2 + 3y^2)$$

plugging in the values:

$$2 \cdot 1 \cdot 2(3^2 + 3(mv^2)^2) = 4(9 + 3(4)^2) = 4(9 + 3 \cdot 16) = 4(9 + 48) = 228$$

OR

$$F(x, m, v) = x^2mv^2 + (mv^2)^3 = x^2mv^2 + m^3v^6$$

$$\frac{dF}{dv} = 2x^2mv + 6m^3v^5 = 2mv(x^2 + 3m^2v^4) = 2mv(x^2 + 3(mv^2)^2) = \text{same as above.}$$

12. Volume of a cylinder.

For a cylinder of radius r and height h , the volume is $V = \pi r^2 h$ and the surface area is $A = 2\pi r^2 + 2\pi r h$.

- Derive the height $h(r_0)$ that maximizes the volume of a cylinder with a given area $A = a_0$ and given radius r_0 .
- Compute the change in volume, ΔV , from $(r_1, h_1) = (1, 1)$ to $(r_2, h_2) = (2, 2)$.
- Compute the component volume changes, ΔV_a and ΔV_b , which sum to ΔV , where ΔV_a is the change from $(r_1, h_1) = (1, 1)$ to $(r_2, h_1) = (2, 1)$ and $(r_2, h_1) = (2, 1)$ to $(r_2, h_2) = (2, 2)$.
- Should (b) equal (c)? Why or why not?

- Use the expression $A = a_0 = 2\pi r_0^2 + 2\pi r_0 h$ to solve for h : $h(r_0) = \frac{a_0 - 2\pi r_0^2}{2\pi r_0} = \frac{a_0}{2\pi r_0} - 1$.

$$\text{Since } V = \pi r_0^2 h, V(a_0, r_0) = \pi r_0^2 \left(\frac{a_0}{2\pi r_0} - 1 \right) = \frac{a_0 r_0}{2} - \pi r_0^2.$$

- $V = \pi r^2 h$

$$\frac{\partial V}{\partial r} = 2\pi r h, \frac{\partial V}{\partial h} = \pi r^2$$

$$\frac{\partial^2 V}{\partial r \partial h} = 2\pi r, \frac{\partial^2 V}{\partial h \partial r} = 2\pi r \implies \text{This is a state function.}$$

$$dV = \frac{\partial V}{\partial r} dr + \frac{\partial V}{\partial h} dh = 2\pi r h dr + \pi r^2 dh$$

$$\int_1^2 \int_1^2 2\pi r h dr + \pi r^2 dh = \pi r^2 h \Big|_{1,1}^{2,2}$$

$$\pi(2^2 \cdot 2 - 1^2 \cdot 1) = \pi(8 - 1)$$

$$\Delta V = 7\pi$$

$$\begin{aligned} \text{(c)} \quad \Delta V_a &= \int_1^2 2\pi r h dr = \left. \frac{2\pi r^2 h}{2} \right|_1^2 = \pi r^2 \cdot 1 \Big|_1^2 = \pi(2^2 - 1^2) = 3\pi \\ \Delta V_b &= \int_1^2 \pi r^2 h dr = \left. \frac{\pi r^2 h}{2} \right|_1^2 = \pi 2^2 \cdot h \Big|_1^2 = 4\pi(2 - 1) = 4\pi \\ \Delta V &= \Delta V_a + \Delta V_b = 3\pi + 4\pi = 7\pi \end{aligned}$$

- (d) Yes, (b) and (c) should be equal. V is a state function, as shown in part (b). Therefore, the path of integration should not affect the final result.

13. Equations of State.

Which of the following could be the total derivative of an equation of state?

$$\text{(a)} \quad \frac{2nRT}{(V-nb)^2} dV + \frac{R(V-nb)}{nb^2} dT$$

$$\text{(b)} \quad -\frac{nRT}{(V-nb)^2} dV + \frac{nR}{V-nb} dT$$

Cross derivatives for equations of state must be equal.

$$\text{(a)} \quad \text{Is } \frac{\partial}{\partial T} \left(\frac{2nRT}{(V-nb)^2} \right) = \frac{\partial}{\partial V} \left(\frac{R(V-nb)}{nb^2} \right) ?$$

$$\frac{2nR}{(V-nb)^2} \neq \frac{R}{nb^2}$$

No, this could not be the total derivative of an equation of state.

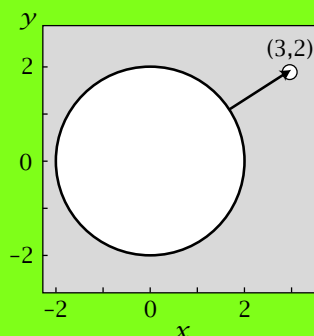
$$\text{(b)} \quad \text{Is } \frac{\partial}{\partial T} \left(-\frac{nRT}{(V-nb)^2} \right) = \frac{\partial}{\partial V} \left(\frac{nR}{V-nb} \right) ?$$

$$-\frac{nR}{(V-nb)^2} = -\frac{nR}{(V-nb)^2}$$

Yes, this could be the total derivative of an equation of state.

14. Distance from the circumference of a circle.

The circle shown below satisfies the equation $x^2 + y^2 = 4$.



Find the point (x^*, y^*) on the circle that is closest to the point $(3, 2)$. (That is, minimizes the distance $f(x, y) = \Delta r^2 = (x - 3)^2 + (y - 2)^2$.)

Minimize the distance $f(x, y) = \Delta r^2 = (x - 3)^2 + (y - 2)^2$ under the constraint $x^2 + y^2 = 4$.

Use Lagrange multipliers.

$$\frac{\partial g}{\partial x} = 2x, \quad \frac{\partial g}{\partial y} = 2y$$

$$\frac{\partial f}{\partial x} = 2(x - 3), \quad \frac{\partial f}{\partial y} = 2(y - 2)$$

The Lagrange method then states that the solution will be given by:

$$\frac{\partial f}{\partial x} = \lambda \left(\frac{\partial g}{\partial x} \right) \implies 2(x - 3) = 2\lambda x \implies \lambda = \frac{x - 3}{x} = 1 - \frac{3}{x}$$

$$\frac{\partial f}{\partial y} = \lambda \left(\frac{\partial g}{\partial y} \right) \implies 2(y - 2) = 2\lambda y \implies \lambda = \frac{y - 2}{y} = 1 - \frac{2}{y}$$

Combining these results with the constraint $x^2 + y^2 = 4$ gives us:

$$\lambda = 1 - \frac{3}{x} = 1 - \frac{2}{y} \implies \frac{3}{x} = \frac{2}{y} \implies x = \frac{3}{2}y$$

$$\left(\frac{3}{2}y\right)^2 + y^2 = 4 \implies \frac{13}{4}y^2 = 4 \implies y^2 = \frac{16}{13} \implies y = \sqrt{\frac{16}{13}} = \frac{4}{\sqrt{13}}$$

$$x = \frac{3}{2} \cdot \frac{4}{\sqrt{13}} = \frac{6}{\sqrt{13}}$$

$$\implies (x^*, y^*) = \left(\frac{6}{\sqrt{13}}, \frac{4}{\sqrt{13}} \right)$$

15. Find df and Δf .

(a) If $f(x, y) = x^2 + 3y$, express df in terms of dx and dy .

(b) For $f(x, y) = x^2 + 3y$, integrate from $(x, y) = (1, 1)$ to $(x, y) = (3, 3)$ to obtain Δf .

(a) $f(x, y) = x^2 + 3y$

$$\frac{\partial f}{\partial x} = 2x, \quad \frac{\partial f}{\partial y} = 3$$

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy = 2x dx + 3 dy$$

$$(b) \quad f(x, y) = x^2 + 3y$$

$$\int_{x=1}^{x=3} df(x, y=1) + \int_{y=1}^{y=3} df(x=3, y) = \int_1^3 2x dx + \int_1^3 3 dy = 3^2 - 1^2 + 3 * 3 - 3 * 1 = 14$$

To check this, $\Delta f = f(3, 3) - f(1, 1) = (3^2 + 3 * 3) - (1^2 - 3 * 1) = (9 + 9) - (1 - 3) = 14$.

16. Derivative of a composite function.

For $f(x, y) = x^2y + y^3$ where $y = mr^2$, find $\frac{df}{dr}$.

$$\frac{df}{dr} = \frac{\partial f}{\partial x} \frac{dx}{dr} + \frac{\partial f}{\partial y} \frac{dy}{dr} \implies \frac{df}{dr} = 2mr(x^2 + 3m^2r^4)$$

17. Maximum volume of a solid with constraints.

You have a rectangular solid of length x , width y , and height z . Derive the values of x , y , and z that give the maximum volume, subject to a fixed surface area: $g(x, y, z) = 2xz + 2yz + 2xy - \text{constant} = 0$.

Use the method of Lagrange multipliers:

$$f(x, y, z) = xyz; \quad g(x, y, z) = 2xz + 2yz + 2xy - \text{constant} = 0$$

$$\frac{\partial f}{\partial x} = \lambda \frac{\partial g}{\partial x} \implies yz = \lambda(2y + 2z)$$

$$\frac{\partial f}{\partial y} = \lambda \frac{\partial g}{\partial y} \implies xz = \lambda(2x + 2z)$$

$$\frac{\partial f}{\partial z} = \lambda \frac{\partial g}{\partial z} \implies xy = \lambda(2x + 2y)$$

$$\frac{1}{2\lambda} = \frac{x+y}{xy} = \frac{x+z}{xz} = \frac{y+z}{yz} \implies \frac{xy+xz}{xyz} = \frac{xy+zy}{xyz} = \frac{xz+yz}{xyz}$$

$$x^* = y^* = z^*$$

18. Short answer questions.

(a) Compute the partial derivatives, $(\frac{\partial f}{\partial x})_y$, $(\frac{\partial f}{\partial y})_x$, for the following functions.

(a) $f(x, y) = \ln(2x) + 5y^3$

(b) $f(x, y) = (x + a)^8 y^{\frac{1}{2}}$

(c) $f(x, y) = \exp^{7y^2} + 9$

(d) $f(x, y) = 13x + 6xy^3$

(b) Which of the following are exact differentials?

(a) $5x^2 dx + 6y dy$

(b) $5 \ln(y) dx + 5x^0 dy$

(c) $(\sin(x) - y \cos(x)) dx + \sin(-x) dy$

(d) $(\exp^{2x} + y) dx + (x + \exp^{2y}) dy$

(e) $y^2 dy + x^2 dx$

(a) (a) $(\frac{\partial f}{\partial x})_y = \frac{1}{x}$, $(\frac{\partial f}{\partial y})_x = 15y^2$

(b) $(\frac{\partial f}{\partial x})_y = 8y^{\frac{1}{2}}(x + a)^7$, $(\frac{\partial f}{\partial y})_x = \frac{(x+a)^8}{2\sqrt{y}}$

(c) $(\frac{\partial f}{\partial x})_y = 0$, $(\frac{\partial f}{\partial y})_x = 14ye^{7y^2}$

(d) $(\frac{\partial f}{\partial x})_y = 13 + 6y^3$, $(\frac{\partial f}{\partial y})_x = 18xy^2$

(b) Exact Differentials

Let $f(x, y) = u(x, y)dx + v(x, y)dy$, where $f(x, y) = dg(x, y)$ if $f(x, y)$ is an exact differential.

	$\frac{\partial u}{\partial y}$	$\frac{\partial v}{\partial x}$	
(a)	0	0	exact
(b)	$\frac{5}{y}$	0	inexact
(c)	$-\cos(x)$	$-\cos(x)$	exact
(d)	1	1	exact
(e)	0	0	exact

Chapter 5

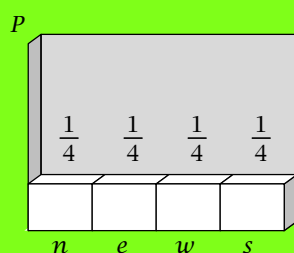
Entropy and the Boltzmann Law

1. Calculating the entropy of dipoles in a field.

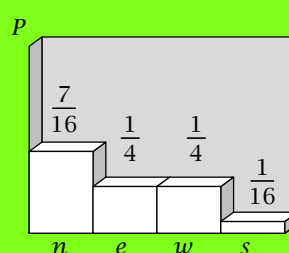
You have a solution of dipolar molecules with a positive charge at the head and a negative charge at the tail. When there is no electric field applied to the solution, the dipoles point north (*n*), east (*e*), west (*w*), or south (*s*) with equal probabilities. The probability distribution is shown in part (a) of the figure below. However when you apply a field to the solution, you now observe a different distribution, with more heads pointing north, as shown in part (b) of the figure below.

- (a) What is the polarity of the applied field? (In which direction does the field have its most positive pole?)
- (b) Calculate the entropy of the system in the absence of the field.
- (c) Calculate the entropy of the system in the applied field.
- (d) Does the system become more ordered or disordered when the field is applied?

(a) Electric Field Absent



(b) Electric Field Present



(a) Since the field causes more “+”-charged heads to point north and fewer south, then it means that the field is negative at the north pole and positive at the south pole.

(b) The entropy is

$$\begin{aligned}
 S/k &= -\sum_{i=1}^4 p(i) \ln p(i) \\
 &= -p_N \ln p_N - p_S \ln p_S - p_E \ln p_E - p_W \ln p_W \\
 &= -[4 \left(\frac{1}{4} \ln \frac{1}{4} \right)] = \ln 4 = 1.386 \\
 S &= 1.386k
 \end{aligned}$$

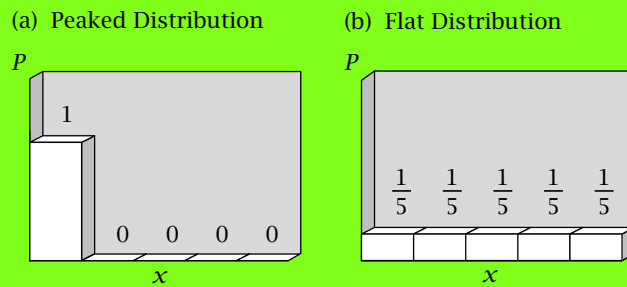
(c) In the presence of the applied field,

$$\begin{aligned}
 \frac{S}{k} &= -\left[\left(\frac{7}{16} \right) \ln \left(\frac{7}{16} \right) + \frac{1}{4} \ln \left(\frac{1}{4} \right) + \frac{1}{4} \ln \left(\frac{1}{4} \right) + \frac{1}{16} \ln \left(\frac{1}{16} \right) \right] \\
 &= 1.228 \quad \text{so} \quad S = 1.228k
 \end{aligned}$$

(d) The entropy is reduced by the applied field, so the system is more ordered.

2. Comparing the entropy of peaked and flat distributions.

Compute the entropies for the spatial concentration shown in figures (a) and (b) below.



$$(a) \quad S/k = -\sum p(i) \ln p(i) = -1 \ln 1 = 0$$

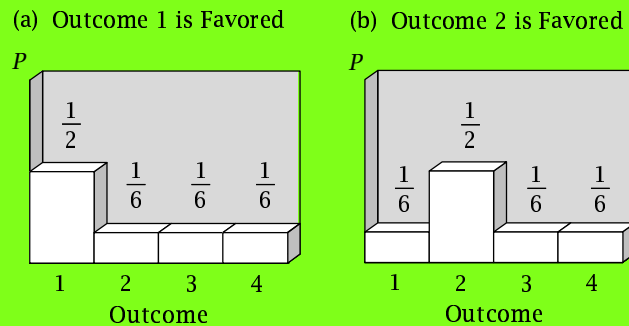
$$(b) \quad S/k = -\sum p(i) \ln p(i) = -5(0.2 \ln 0.2) = \ln 5 = 1.609$$

Thus the entropy is greater for distribution (b). Concentration gradients tend to become

smoother and more uniform over time as a result of trying to maximize entropy.

3. Comparing the entropy of two peaked distributions.

Which of the two distributions shown in the figure below has the greater entropy?



Both have the same entropy. For either one $S/k = -\sum_{i=1}^4 p(i) \ln p(i)$

$$\begin{aligned}
 &= -\left[\frac{1}{6} \ln \frac{1}{6} + \frac{1}{6} \ln \frac{1}{6} + \frac{1}{6} \ln \frac{1}{6} + \frac{1}{2} \ln \frac{1}{2}\right] \\
 &= \frac{1}{2} \ln 6 + \frac{1}{2} \ln 2 = \frac{1}{2} \ln 12 = 1.242
 \end{aligned}$$

4. Calculating the entropy of mixing.

Consider a lattice with N sites and n green particles. Consider another lattice, adjacent to the first, with M sites and m red particles. Assume that the green and red particles cannot switch lattices. This is state A .

- What is the total number of configurations W_A of the system in state A ?
- Now assume that all $N + M$ sites are available to all the green and red particles. The particles remain distinguishable by their color. This is state B . Now what is the total number of configurations W_B of the system?

Now take $N = M$ and $n = m$ for the following two problems.

- (c) Using Stirling's approximation, what is the ratio W_A/W_B ?
- (d) Which state, A or B , has the greatest entropy? Calculate the entropy difference given by

$$\Delta S = S_A - S_B = k \ln \left(\frac{W_A}{W_B} \right).$$

- (a) Since the two lattices are independent: $W_a = W_N W_M = \frac{N!}{n!(N-n)!} \frac{M!}{m!(M-m)!}$

- (b) $W_b = \frac{(N+M)!}{n!m!(N+M-n-m)!}$

- (c) $\frac{W_a}{W_b} = \frac{(N!)^2 (2N-2n)!}{(2N)! [(N-n)!]^2} \approx \frac{N^2 N (2N-2n)^2 N - 2n}{(2N)^2 N (N-n)^2 N - 2n} = \frac{2^{2N-2n}}{2^{2N}} = 2^{-2n}$

- (d) $\Delta S = k \ln \left(\frac{W_a}{W_b} \right) = k \ln 2^{-2n} = -nk \ln 4$

There is greater entropy in B , when all the particles are unconstrained and have access to the full volume.

5. Proof of maximum entropy for two outcomes.

Example 6.4 is simple enough that you can prove the answer is correct even without using the maximum entropy principle. Show this.

Let p_H be the probability of the outcome tails, and p_T the probability of heads. Because they are probabilities, we require $p_H + p_T = 1$. Let $\varepsilon_T = 1$, $\varepsilon_H = 2$. Then $\langle \varepsilon \rangle = p_T + 2p_H$. We therefore have a system of two equations

$$p_T + 2p_H = \langle \varepsilon \rangle \quad p_T + p_H = 1$$

with two unknowns, p_T and p_H . Subtracting the two equations gives us $p_H = \langle \varepsilon \rangle - 1$ and $p_T = 1 - p_H = 1 - \langle \varepsilon \rangle + 1 = 2 - \langle \varepsilon \rangle$.

For $\langle \varepsilon \rangle = 1.5$, $p_T = p_H = 0.5$, but for $\langle \varepsilon \rangle = 1.2$, $p_T = 0.8$, $p_H = 0.2$.

6. Other definitions of entropy don't satisfy the product rule.

In contrast to problem 6, show that if the entropy were defined by a least-squares criterion, as $S/k = \sum_{i=1}^t p_i^2$, the multiplication rule would not be satisfied when S is maximal.

The table used for Problem 6 applies, but now the entropy would be

$$\frac{S}{k} = q^2 + (u_1 - q)^2 + (v_1 - q)^2 + (v_2 - u_1 + q)^2$$

and

$$\begin{aligned} \left(\frac{\partial(S/k)}{\partial q} \right) &= 2[q - (u_1 - q) - (v_1 - q) + (v_2 - u_1 + q)] = 0 \\ \implies 4q &= 2u_1 + v_1 - v_2 \end{aligned}$$

which does not give $q = u_1 v_1$, as we expected.

7. The maximum entropy distribution is Gaussian when the second moment is given.

Prove that the probability distribution p_i that maximizes the entropy for die rolls subject to a constant value of the second moment $\langle i^2 \rangle$ is a Gaussian function. Use $\varepsilon_i = i$.

Maximize the entropy subject to two constraints,

$$\begin{aligned} \sum_{i=1}^t p_i &= 1 \\ \sum_{i=1}^t i^2 p_i &= \langle i^2 \rangle = \alpha. \end{aligned}$$

Now Equation (6.11) becomes

$$(a) \quad -1 - \ln p_i^* - \lambda - \beta i^2 = 0 \implies p_i^* = e^{-1-\lambda-\beta i^2}.$$

Dividing both sides of Equation (a) by

$$\sum_{i=1}^t e^{-1-\lambda-\beta i^2}$$

gives

$$p_i^* = \frac{e^{-\beta i^2}}{\sum_{i=1}^t e^{-\beta i^2}}$$

which is a gaussian function of i .

8. Maximum entropy for three-sided die.

You have a three-sided die, with numbers **1**, **2** and **3** on the sides. For a series of N dice rolls, you observe an average score α per roll using the maximum entropy principle.

- Write expressions that show how to compute the relative probabilities of occurrence of the three sides, n_1^*/N , n_2^*/N , and n_3^*/N , if α is given.
- Compute n_1^*/N , n_2^*/N , and n_3^*/N if $\alpha = 2$.
- Compute n_1^*/N , n_2^*/N , and n_3^*/N , if $\alpha = 1.5$.
- Compute n_1^*/N , n_2^*/N , and n_3^*/N if $\alpha = 2.5$.

$$(a) \quad \frac{n_i^*}{N} = \frac{x^i}{q} \quad q = x + x^2 + x^3 \quad \alpha = \frac{x + 2x^2 + 3x^3}{x + x^2 + x^3} = \frac{1 + 2x + 3x^2}{1 + x + x^2}.$$

$\implies (3 - \alpha)x^2 + (2 - \alpha)x + (1 - \alpha) = 0$. Use quadratic equation

$$x = \frac{(\alpha - 2) \pm [(2 - \alpha)^2 - 4(1 - \alpha)(3 - \alpha)]^{1/2}}{2(3 - \alpha)}.$$

$$(b) \quad \alpha = 2 \implies \frac{n_1^*}{N} = \frac{n_2^*}{N} = \frac{n_3^*}{N} = \frac{1}{3}.$$

$$(c) \quad \alpha = 1.5 \implies \frac{n_1^*}{N} = 0.62 \quad \frac{n_2^*}{N} = 0.27 \quad \frac{n_3^*}{N} = 0.11.$$

$$(d) \quad \alpha = 2.5 \implies \frac{n_1^*}{N} = 0.11 \quad \frac{n_2^*}{N} = 0.27 \quad \frac{n_3^*}{N} = 0.62.$$

9. Maximum entropy in Las Vegas.

You play a slot machine in Las Vegas. For every \$1 coin you insert, there are three outcomes: (1) you lose \$1, (2) you win \$1, so your profit is \$0, (3) you win \$5, so your profit is \$4. Suppose you find that your average expected profit over many trials is \$0 (what an optimist!). Find the maximum entropy distribution for the probabilities p_1 , p_2 , and p_3 of observing each of these three outcomes.

We have three possible payoffs, $f_1 = -1$ (we don't win anything and so have lost \$1), $f_2 = 0$ (we win \$1 for a net profit of zero), and $f_3 = 4$ (we win \$5 for a net profit of \$4). If each of these possible outcomes has associated with it a probability p_i , then the expected net profit will be given by:

$$\langle f \rangle = f_1 p_1 + f_2 p_2 + f_3 p_3.$$

Let $x = e^{-\beta}$. Then $p_i = x^{f_i}/q$ where $q = x^{f_1} + x^{f_2} + x^{f_3} = x^{-1} + x^0 + x^4$ and

$$\begin{aligned}\langle f \rangle &= \frac{-1x^{-1} + 0x^0 + 4x^4}{x^{-1} + x^0 + x^4} = 0 \\ \implies -\frac{1}{x} + 4x^4 &= 0 \implies 4x^5 = 1 \implies x = 0.758.\end{aligned}$$

So you have

$$\begin{aligned}p_i &= \frac{e^{-\beta f_i}}{q} = \frac{x^{f_i}}{q} \\ q &= \left(\frac{1}{0.758}\right) + 1 + (0.758)^4 \\ q &= 2.65.\end{aligned}$$

The probabilities of the outcomes are therefore:

$$\begin{aligned}p_1 &= \frac{x^{-1}}{q} = 0.498 \\ p_2 &= \frac{x^0}{q} = 0.377\end{aligned}$$

$$p_3 = \frac{x^4}{q} = 0.125$$

10. Flat distribution, high entropy.

For four coin flips, for each distribution of probabilities, $(p_H, p_T) = (0, 1), (1/4, 3/4), (1/2, 1/2), (3/4, 1/4), (1, 0)$, compute W , and show that the flattest distribution has the highest multiplicity.

- (a) For $(p_H, p_T) = (0, 1)$ or $(1, 0)$, $W = \frac{4!}{0!4!} = 1$.
- (b) For $(p_H, p_T) = (1/4, 3/4)$ or $(3/4, 1/4)$, $W = \frac{4!}{1!3!} = 4$.
- (c) For $(p_H, p_T) = (1/2, 1/2)$, $W = \frac{4!}{2!2!} = 6$.

Therefore the flattest distribution of probabilities, (c), corresponds to the highest multiplicity.

Chapter 6

Thermodynamic Driving Forces

1. One dimensional lattice.

You have a 1-dimensional lattice that contains N_A particles of type A and N_B particles of type B . They completely fill the lattice, so the number of sites is $N_A + N_B$.

- (a) Express the entropy $S(N_A, N_B)$ as a function of N_A and N_B .
- (b) Give the relationship between the chemical potential μ_A and the quantity $\left(\frac{\partial S}{\partial N_A}\right)_{N_B}$.
- (c) Express $\mu_A(N_A, N_B)$.

$$(a) \quad W(N_A, N_B) = \frac{(N_A + N_B)!}{N_A! N_B!},$$

$$S = k \ln W = k [(N_A + N_B) \ln(N_A + N_B) - N_A \ln N_A - N_B \ln N_B].$$

$$(b) \quad dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu_A}{T} dN_A - \frac{\mu_B}{T} dN_B,$$

$$\frac{\mu_A}{T} = - \left(\frac{\partial S}{\partial N_A} \right)_{N_B, U, V}.$$

$$(c) \quad \left(\frac{\partial S}{\partial N_A} \right)_{N_B} = k [\ln(N_A + N_B) + 1 - \ln N_A - 1] = -k \ln \frac{N_A}{N_A + N_B},$$

$$\mu_A = kT \ln \frac{N_A}{N_A + N_B} = kT \ln C,$$

where C is the mole fraction concentration of A 's in B 's.

2. The entropy of an ideal gas.

Show that the entropy for an ideal gas is

$$S(V, N) = Nk \ln V.$$

Using Equation (6.6) we have

$$\left(\frac{\partial S}{\partial V} \right)_{U, N} = \frac{p}{T} = \frac{Nk}{V}.$$

Rearranging and integrating gives $dS = Nk \int \frac{dV}{V}$

$$\implies \Delta S = S_2 - S_1 = Nk \ln \left(\frac{V_2}{V_1} \right).$$

3. Entropy changes don't depend on a process pathway.

For an ideal gas, the entropy is $S = Nk \ln V$ (see above).

- (a) Express $\Delta S_V = S_2(V_2) - S_1(V_1)$, the entropy change upon changing the volume from V_1 to V_2 , at fixed particle number N .
- (b) Express $\Delta S_N = S_2(N_2) - S_1(N_1)$, the entropy change upon changing the particle number from N_1 to N_2 , at fixed volume V .
- (c) Write an expression for the entropy change, ΔS , for a two-step process $(V_1, N_1) \rightarrow (V_2, N_1) \rightarrow (V_2, N_2)$ in which the volume changes first at fixed particle number, then the particle number changes at fixed volume.
- (d) Show that the entropy change ΔS above is exactly the same as for the two-step process in reverse order: changing the particle number first, then the volume.

(a) $\Delta S = Nk \ln \left(\frac{V_2}{V_1} \right).$

(b) $\Delta S = (N_2 - N_1)k \ln V.$

(c)

$$\begin{aligned}\Delta S &= N_1 k \ln\left(\frac{V_2}{V_1}\right) + (N_2 - N_1)k \ln V_2 \\ &= k[N_1 \ln V_2 - N_1 \ln V_1 + N_2 \ln V_2 - N_1 \ln V_2] \\ &= k[N_2 \ln V_2 - N_1 \ln V_1].\end{aligned}$$

(d)

$$\begin{aligned}\Delta S &= (N_2 - N_1)k \ln V_1 + N_2 k \ln\left(\frac{V_2}{V_1}\right) \\ &= k[N_2 \ln V_2 - N_1 \ln V_1].\end{aligned}$$

4. Compute $\Delta S(V)$ for an ideal gas.

What is the entropy change if you double the volume from V to $2V$ in a quasi-static isothermal process at temperature T ?

$$\Delta S = S_2 - S_1 = Nk \ln\left(\frac{2V}{V}\right) = Nk \ln 2.$$

Chapter 7

The Logic of Thermodynamics

1. The work of compression.

One mole of a van der Waals gas is compressed quasi-statically and isothermally from volume V_1 to V_2 . For a van der Waals gas, the pressure is

$$p = \frac{RT}{V-b} - \frac{a}{V^2},$$

where a and b are material constants, V is the volume and RT is the gas constant \times temperature.

- (a) Write the expression for the work done.
- (b) Is more or less work required than in the low-density limit than for an ideal gas? What about the high-density limit? Why?

- (a) $w = - \int_{V_1}^{V_2} p_{\text{ext}} dV$ In a quasi-static process

$$p_{\text{ext}} = p_{\text{gas}} = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$w = \int_{V_1}^{V_2} \left[\left(\frac{-RT}{V-b} \right) + \left(\frac{a}{V^2} \right) \right] dV = -RT \ln \left(\frac{V_2-b}{V_1-b} \right) - a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

- (b) For large volumes, the logarithm term is small and for

$$V_2 < V_1, \quad -a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) < 0.$$

Therefore *less* work is required to compress a real gas. The van der Waals gas has internal attractive energy which aids compression. On the other hand, when the

volumes are small (high densities), then the logarithm term is dominant and the van der Waals gas has stronger repulsion; in that case *more* work is required to compress it than an ideal gas.

2. Deriving the ideal gas law in two dimensions.

Molecules at low density on a surface, such as surfactants at an interface of air and water, often obey a two-dimensional equivalent of the ideal gas law. The two-dimensional equivalent of p is π , where π is a lateral two-dimensional pressure. A is area. Using

$$\pi = T \left(\frac{\partial S}{\partial A} \right)_N \quad (7)$$

and assuming no energetic interactions, derive the two-dimensional equivalent of the ideal gas law by using a lattice model in the low-density limit.

As in the three-dimensional problem, we consider the N molecules randomly distributed on a lattice of M sites. In this case, we use a two-dimensional lattice. There are M possible placements of the first particle, $M - 1$ possible placements for the second particle, $M - 2$ for the third, and so on. Therefore the number of arrangements, W , is

$$W = \frac{(M!)}{(M - N)!N!}$$

We use the Boltzmann equation

$$S = k \ln W = k \ln \left[\frac{M!}{(M - N)!N!} \right]$$

and Stirling's approximation ($x! \approx (\frac{x}{e})^x$) to get:

$$S = k \ln \left[\frac{M^M}{(M - N)^{M - N} N^N} \right] = -k \left[N \ln \left(\frac{N}{M} \right) + (M - N) \ln \left(\frac{M - N}{M} \right) \right]$$

Using the thermodynamic expression given in the problem,

$$\Pi = T \left[\frac{\partial S}{\partial A} \right]_{U, N}; \quad \text{also} \quad \left[\frac{\partial S}{\partial A} \right]_{U, N} = \left(\frac{\partial S}{\partial M} \right) \left(\frac{\partial M}{\partial A} \right)$$

so we calculate each term

$$\begin{aligned}
 \left(\frac{\partial S}{\partial M} \right) &= k \left[\frac{N}{M} + \frac{M-N}{M} - 1 + \ln M - \ln(M-N) \right] \\
 &= k \ln \left(\frac{M}{M-N} \right) \\
 &= -k \ln \left(1 - \frac{N}{M} \right) \\
 \left(\frac{\partial M}{\partial A} \right) &= \frac{M}{A};
 \end{aligned}$$

At low densities,

$$N \ll M, \text{ so } \frac{N}{M} \ll 1,$$

and therefore

$$\Pi = -kT \left(\frac{M}{A} \right) \ln \left(1 - \frac{N}{M} \right) \approx \frac{NkT}{A},$$

since

$$\ln \left(1 - \frac{N}{M} \right) \approx -\frac{N}{M} + \dots$$

This is the two-dimensional ideal gas law.

3. The work of expansion in freezing an ice cube.

At 1 atm, freeze an amount of liquid water that is $2 \text{ cm} \times 2 \text{ cm} \times 2 \text{ cm}$ in volume. The density (mass per unit volume) of liquid water at 0°C is 1.000 g cm^{-3} and the density of ice at 0°C is 0.915 g cm^{-3} .

- (a) What is the work of expansion upon freezing?
- (b) Is work done *on* the system or *by* the system?

At constant external pressure, $p_{\text{ext}} = 1 \text{ atm}$, the work is given by Equation (7.37).

$$\begin{aligned}
 w &= -p_{\text{ext}}(V_{\text{ice}} - V_{\text{liquid water}}) \\
 &= -p_{\text{ext}} \left(\frac{m_{\text{ice}}}{\rho_{\text{ice}}} - \frac{m_{\text{liquid}}}{\rho_{\text{liquid}}} \right) \\
 &= -(1 \text{ atm})(8 \text{ g}) \left(\frac{1}{0.915 \text{ g cm}^{-3}} - \frac{1}{1 \text{ g cm}^{-3}} \right) \left(2.422 \times 10^{-2} \frac{\text{cal}}{\text{cm}^3 \text{ atm}} \right) \\
 &= -0.018 \text{ cal}
 \end{aligned}$$

Since the sign is negative, this work is done by the system expanding against the atmosphere.

4. The work of expanding a gas.

Compute the total work performed when expanding an ideal gas, at constant temperature, from volume V to $2V$.

The work is given by Equation (7.42)

$$w = -NkT \ln \left(\frac{2V}{V} \right) = -NkT \ln 2.$$

5. Pulling out the partition between two chambers of a gas.

A partition separates equal volumes containing equal numbers N of ideal gas molecules of the same species at the same temperature. Using a simple lattice model for ideal gases, evaluate the relevant multiplicity terms to show that the entropy of the composite system does not change when the partition is removed (hint: use Stirling's approximation).

Let 1 refer to the left side, and 2 refer to the right side. Before removing the partition, composite $W = W_1 W_2$. Since each side is identical, $W(\text{before}) = W_1^2$. $W_1 = M!/(N!(M-N)!)$ where M is the number of lattice sites and N is the number of particles. Using Stirling's approximation, we can write

$$W_1 = \frac{\left(\frac{M}{e}\right)^M}{\left(\frac{N}{e}\right)^N \left(\frac{M-N}{e}\right)^{M-N}} = \frac{M^M}{N^N (M-N)^{M-N}} \quad \text{so}$$

$$W(\text{before}) = W_1^2 = \frac{M^{2M}}{N^{2N}(M-N)^{2M-2N}}.$$

After removing the partition, there are $2M$ lattice sites and $2N$ particles. This leads to

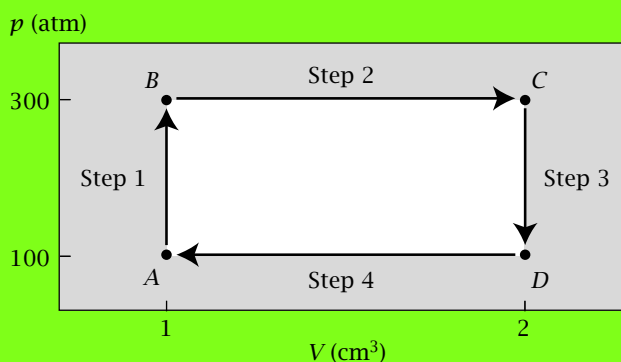
$$\begin{aligned} W(\text{after}) &= \frac{(2M)!}{(2N)!(2M-2N)!} = \frac{\left(\frac{2M}{e}\right)^{2M}}{\left(\frac{2N}{e}\right)^{2N} \left(\frac{2M-2N}{e}\right)^{2M-2N}} \\ &= \frac{M^{2M}}{N^{2N}(M-N)^{2M-2N}} = W_1^2. \end{aligned}$$

Note that the factors $(2/e)$ all cancel out in the above expression, in the same manner that the factor $(1/e)$ cancels out in the equation for W_1 . Thus $W(\text{after}) = W(\text{before})$ and since $S = k \ln W$, we have $S(\text{after removing partition}) = S(\text{before removing partition})$ and thus

$$\Delta S = k \ln \frac{W(\text{after})}{W(\text{before})} = k \ln 1 = 0.$$

6. The work in a thermodynamic cycle.

A thermodynamic cycle is a series of steps that ultimately returns to its beginning point. Compute the total work performed around the thermodynamic cycle of quasi-static processes in the figure below.



Using Equation (7.36), we have

$$\begin{aligned} W &= -\int_A^B p \, dV - \int_B^C p \, dV - \int_C^D p \, dV - \int_D^A p \, dV \\ &= 0 - (300 \text{ atm})(2 \text{ cm}^3 - 1 \text{ cm}^3) - 0 - (100 \text{ atm})(1 \text{ cm}^3 - 2 \text{ cm}^3) \\ &= -(200 \text{ atm cm}^3) \times (2.422 \times 10^{-2} \text{ cal}/(\text{cm}^3 \text{ atm})) = -4.84 \text{ cal} \end{aligned}$$

Since steps 1 and 3 involve no volume change, there is no work performed during those steps.

7. Engine efficiencies.

Consider a Carnot engine that runs at $T_h = 380$ K.

- (a) Compute the efficiency if $T_c = 0^\circ\text{C} = 273$ K.
- (b) Compute the efficiency if $T_c = 50^\circ\text{C} = 323$ K.

Equation (7.45) gives

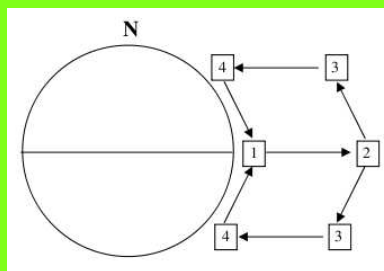
$$\eta = 1 - \frac{T_c}{T_h}.$$

- (a) $\eta = 1 - \frac{273}{380} = 28\%$ efficient
- (b) $\eta = 1 - \frac{323}{380} = 15\%$ efficient

Big difference!

8. Hadley Cycles - what powers the trade winds?

The Earth's trade winds arise from the differences in buoyancy between hot air and cold air. Air is heated at the Earth's surface near the equator (see (1) in figure below), lowering its density; it rises (2), pushing upper air away toward the Northern latitudes where the air cools (3), then drops back down to Earth (4), pushing the cold surface air back toward the equator.



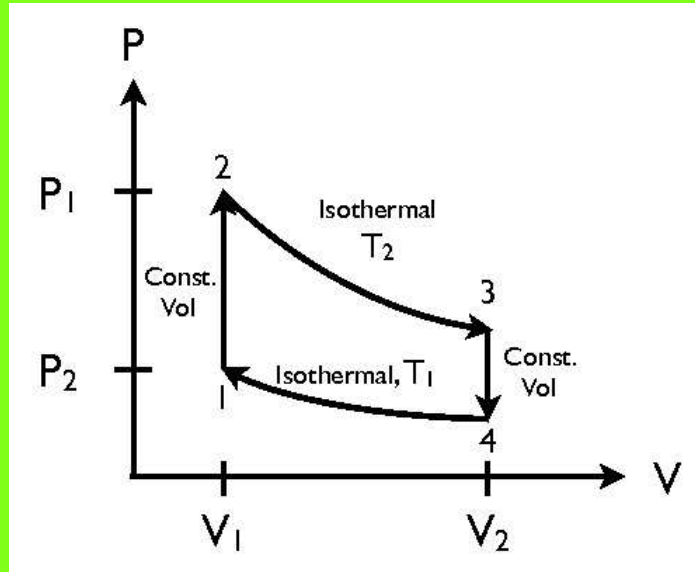
Consider an imaginary balloon containing 1 m^3 of an ideal gas.

- (a) At $p = 1 \text{ atm}$ and $T = 300 \text{ K}$, what is the number of moles n of air contained in the balloon?
- (b) If that balloon of n moles of air remains at $p = 1 \text{ atm}$ but is now heated to $T = 330 \text{ K}$, its volume increases. What is the new density, $\rho = n/V$?
- (c) Assuming no heat transfer, how high will the balloon in part (b) rise? Use Figure 10.2 in the book to make a rough guess. (Useful conversion: $1 \text{ atm} \approx 1 \text{ bar}$)

- (a) Use the ideal gas law: $p = \frac{nRT}{V}$
 so $n = \frac{pV}{RT} = \frac{(1\text{atm})(1\text{m}^3)(\frac{1\text{liter}}{10^{-3}\text{m}^3})}{(8.21 \cdot 10^{-2} \frac{\text{liter} \cdot \text{atm}}{\text{K} \cdot \text{mol}})(300\text{K})}$
 $n = 40.6 \text{ moles}$
- (b) Using the ideal gas law in the form: $p = \rho RT$, we have
 $\rho_1 T_1 = \frac{p}{R} = \rho_2 T_2 \implies \frac{\rho_2}{\rho_1} = \frac{T_1}{T_2}$
 $\implies \rho_2 = (\frac{300}{330})\rho_1 = (\frac{300}{330})(\frac{40.6 \text{ moles}}{\text{m}^3}) = 36.9 \frac{\text{moles}}{\text{m}^3}$
- (c) $p \approx \frac{300}{330} \approx 0.9 \text{ atm}$ is at an altitude of $\sim 1 \text{ mile}$.

9. Stirling Engine.

A Stirling engine has the following pV cycle and uses an ideal gas working fluid. The steps are quasi-static.



- (a) How much work is done in the constant volume segments, W_{12} and W_{34} ?
- (b) What is the energy change around the cycle, $\Delta U_{tot} = \Delta U_{12} + \Delta U_{23} + \Delta U_{34} + \Delta U_{41}$?
- (c) What is the total work performed around the cycle, $W_{tot} = W_{12} + W_{23} + W_{34} + W_{41}$?
- (d) If $T_2 = 2000K$, $T_1 = 300K$, $V_2 = 1L$, $V_1 = 0.01L$ and $n = 0.1$ mole of ideal gas, compute W_{tot} .

(a) Constant volume $\implies w = 0$

(b) U is a state function, so $\Delta U_{tot} = 0$

(c) $w_{12} = 0 = w_{34}$

$$w_{23} = -\int_{V_1}^{V_2} p dV = -NkT_2 \int_{V_1}^{V_2} \frac{1}{V} dV = -NkT_2 \ln\left(\frac{V_2}{V_1}\right) \text{ for an ideal gas}$$

$$w_{41} = -\int_{V_2}^{V_1} p dV = -NkT_1 \int_{V_2}^{V_1} \frac{1}{V} dV = -NkT_1 \ln\left(\frac{V_1}{V_2}\right)$$

$$w_{tot} = -NkT_2 \ln\left(\frac{V_2}{V_1}\right) - NkT_1 \ln\left(\frac{V_1}{V_2}\right)$$

(d) $T_2 = 2000K$, $T_1 = 300K$, $V_2 = 1L$, $V_1 = 0.01L$ and $n = 0.1$ mole of ideal gas

$$w_{tot} = -(0.1 \text{ mol})\left(\frac{8.314J}{K \cdot \text{mol}}\right)(2000K) \ln\left(\frac{1L}{0.01L}\right) - (0.1 \text{ mol})\left(\frac{8.314J}{K \cdot \text{mol}}\right)(300K) \ln\left(\frac{0.01L}{1L}\right) \\ \approx -7657.5 + 1148.6 = -6508.9J = -1555.7 \text{ cal}$$

10. Ideal efficiency of a car engine.

Suppose the compression ratio in your car engine is $V_2/V_1 = 8$. For a diatomic gas $C_V = (5/2)Nk$ and for ethane $C_V \approx 5Nk$.

- (a) What is the efficiency of your engine if you burn a diatomic gas?
- (b) Which is more efficient: a diatomic gas or ethane?
- (c) Would your engine be more or less efficient with a higher compression ratio?

- (a) Use Equation 8.53,

$$\eta = 1 - \left(\frac{V_1}{V_2}\right)^{(Nk)/C_V} = 1 - \left(\frac{1}{8}\right)^{0.4} \cong 0.56.$$

- (b) For ethane,

$$\eta = 1 - \left(\frac{1}{8}\right)^{0.2} = 0.34,$$

so it is less efficient than a diatomic gas.

- (c) Higher compression ratios lead to higher efficiency.

Chapter 8

Laboratory Conditions and Free Energies

1. Finding a fundamental equation.

While the Gibbs free energy G is the fundamental function of the natural variables (T, p, \mathbf{N}) , growing biological cells often regulate not the numbers of molecules \mathbf{N} , but the chemical potentials μ_i . That is, they control *concentrations*. What is the fundamental function Z of natural variables (T, p, μ) ?

Start with $G = G(T, p, N)$, and its differential form:

$$dG = -SdT + Vdp + \mu dN \qquad -d(\mu N) = -Nd\mu - \mu dN$$

so

$$d(G - \mu N) = -SdT + Vdp - Nd\mu$$

and the fundamental function is $Z = G - \mu N$.

2. Why does increasing temperature increase disorder?

Systems become disordered as the temperature is increased. For example, liquids and solids become gases, solutions mix, adsorbates desorb. Why?

Increasing temperature increases disorder, because the entropy dominates the free energy at

high temperatures, whereas enthalpy dominates at low temperatures. That is, in the expression

$$\Delta G = \Delta H - T\Delta S,$$

the entropy term ($T\Delta S$) becomes more important (either for ΔS positive or ΔS negative) as T increases, hence at high temperatures the system will become more disordered to increase its entropy, even at the cost of increasing enthalpy.

3. The difference between the energy and enthalpy changes in expanding an ideal gas.

How much heat is required to cause the quasi-static isothermal expansion of one mole of an ideal gas at $T = 500$ K from $P_A = 0.42$ atm, $V_A = 100$ liters to $P_B = 0.15$ atm?

- (a) What is V_B ?
- (b) What is ΔU for this process?
- (c) What is ΔH for this process?

- (a) For an ideal gas, in *any* isothermal process $\Delta U = 0$. Therefore

$$\Delta U = q + w = 0 \implies q = -w.$$

For such a process, when it is also quasi-static:

$$w = - \int p dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1}$$

so

$$\begin{aligned} q &= nRT \ln \left(\frac{V_2}{V_1} \right) \\ &= (1 \text{ mole}) \left(2 \frac{\text{cal}}{\text{mol} \cdot \text{deg}} \right) (500^\circ \ln \left(\frac{V_2}{100\text{l}} \right)) \end{aligned}$$

Using the ideal gas law:

$$p_1 V_1 = nRT = p_2 V_2 \implies \frac{V_2}{V_1} = \frac{p_1}{p_2}$$

Therefore, we can write

$$\begin{aligned} q &= nRT \ln \frac{p_1}{p_2} \\ &= (1000 \text{ cal}) \ln \left(\frac{0.42 \text{ atm}}{0.15 \text{ atm}} \right) \\ &= 1030 \text{ cal} \approx 1000 \text{ cal.} \end{aligned}$$

(b) From the ideal gas law:

$$\begin{aligned} V_2 &= \frac{p_1}{p_2} V_1 = \left(\frac{0.42 \text{ atm}}{0.15 \text{ atm}} \right) (100 \text{ L}) \\ &= 280 \text{ liters} \end{aligned}$$

(c) For any isothermal process of an ideal gas

$$\Delta U = 0 \quad [\Delta U = C_v(T_2 - T_1)]$$

(d) For any isothermal process of an ideal gas

$$\Delta H = 0$$

This can be shown as follows. $\Delta H = \Delta U + \Delta(pV)$. But $\Delta U = 0$; $\Delta(pV) = p_2 V_2 - p_1 V_1$. Using the ideal gas law

$$\begin{aligned} P_2 V_2 &= nRT \\ P_1 V_1 &= nRT \end{aligned}$$

Therefore

$$\begin{aligned} \Delta H &= 0 + (nRT - nRT) \\ &= 0. \end{aligned}$$

4. The work and the heat of boiling water.

For the reversible boiling of five moles of liquid water to steam at 100°C and 1 atm pressure, calculate q . Is w positive or negative?

From tables that give the heat of vaporization of water,

$$\begin{aligned}q_{\text{boiling}} &= -q_{\text{condensation}} = -\Delta H_{\text{condensation}} \\&= \left(540 \frac{\text{cal}}{\text{g}}\right) \left(18 \frac{\text{g}}{\text{mole}}\right) (5 \text{ moles}) \\&= 48,600 \text{ cal} \\q_{\text{boil}} &= 48.6 \text{ kcal}\end{aligned}$$

At constant pressure,

$$\begin{aligned}w &= -\int_{V_1}^{V_2} p dV \\&= -p(V_2 - V_1) = -p(V_{\text{gas}} - V_{\text{liquid}})\end{aligned}$$

so

$$V_{\text{gas}} \gg V_{\text{liquid}} \implies V_{\text{gas}} - V_{\text{liquid}}$$

is positive, so

$$w < 0.$$

5. The entropy and free energy of gas expansion.

Two moles of an ideal gas undergo an irreversible isothermal expansion from $V_A = 100$ liters to $V_B = 300$ liters at $T = 300$ K.

- (a) What is the entropy change for this process?
- (b) What is the Gibbs free energy change?

(a)
$$\Delta S = \int \frac{dq_{\text{rev}}}{T}.$$

Since S and U are state functions, we needn't be concerned that the actual process is irreversible (read: complicated). We can choose *any* path to calculate state functions so we invent an isothermal, quasi-static process to get q_{rev} .

$$\Delta U = 0 \implies q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \frac{V_2}{V_1}.$$

For an isothermal process,

$$\Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1} = (2\text{moles}) \left(2 \frac{\text{cal}}{\text{mol deg}} \right) \ln \frac{300}{100} = 4.39 \frac{\text{cal}}{\text{deg}}$$

(b) $\Delta G = \Delta H - T\Delta S$. For an isothermal process on an ideal gas, $\Delta H = 0$.

(Note that $\Delta H = \Delta U + \Delta(PV)$: For an isothermal process, $\Delta U = 0$

and $\Delta(PV) = \Delta(nRT) = 0$, therefore $\Delta H = 0$).

$$\Delta G = -T\Delta S = -(300\text{K}) \left(4.39 \frac{\text{cal}}{\text{deg}} \right) = -1318.33 \text{ cal}$$

6. The free energy and entropy of membrane melting.

Pure membranes of dipalmitoyl lecithin phospholipids are models of biological membranes. They melt at $T_m = 41^\circ \text{C}$. Reversible melting experiments indicate that $\Delta H_m = 9 \text{ kcal mol}^{-1}$. Calculate

- (a) the entropy of melting ΔS_m , and
- (b) the free energy of melting ΔG_m .
- (c) Does the membrane become more or less ordered upon melting?
- (d) There are 32 rotatable $\text{CH}_2\text{-CH}_2$ bonds in each molecule. What is the increase in multiplicity on melting one mole of bonds?

- (a) For a phase transition,

$$\begin{aligned}\Delta S_m &= \frac{\Delta H_m}{T_m} \\ &= \frac{9 \text{ kcal/mol}}{(273 + 41)\text{K}} \\ &= 28.66 \frac{\text{cal}}{\text{mol K}}\end{aligned}$$

- (b) For reversible phase transitions, the two phases are in equilibrium, therefore

$$\Delta G_m = 0$$

- (c) $\Delta S > 0$, therefore the entropy increases, thus the disorder also increases.

$$\begin{aligned}\text{(d)} \quad \frac{\Delta S_m \text{ cal}}{\text{mol bonds} \cdot \text{K}} &= \frac{\Delta S_m \text{ cal}}{\text{mol lipids} \cdot \text{K}} \left(\frac{1 \text{ mol lipids}}{n_B \text{ mol bonds}} \right) \\ &= \left(\frac{N_A \text{ bonds}}{\text{mol bonds}} \right) \left(\frac{k \text{ J}}{\text{K}} \right) \left(\frac{\text{cal}}{4.184 \text{ J}} \right) \ln \left(\frac{W_{\text{fluid}}}{W_{\text{solid}}} \right)\end{aligned}$$

so

$$\begin{aligned}\frac{W_{\text{fluid}}}{W_{\text{solid}}} &= \exp \left[\frac{\Delta S_m}{Nk n_B} \right] \\ &= \exp \left[\left(\frac{28.66 \text{ cal}}{\text{mol lipids} \cdot \text{K}} \right) \right. \\ &\quad \left. \left(\frac{1 \text{ mol lipids}}{n_B \text{ mol bonds}} \right) (1 \text{ mol bonds}) \left(\frac{\text{K}}{1.381 \cdot 10^{-23} \text{ J}} \right) \left(\frac{4.184 \text{ J}}{\text{cal}} \right) \right]\end{aligned}$$

$$\implies \log \left(\frac{W_{\text{fluid}}}{W_{\text{solid}}} \right) \approx 2.713 \cdot 10^{23}$$

7. State and path dependent functions.

Which quantities sum to zero around a thermodynamic cycle?

- (a) q , heat
- (b) w , work
- (c) $-pdV$
- (d) U
- (e) G

State functions sum to zero around a thermodynamic cycle. That includes (d) U and (e) G , but not heat and work (a), (b) or (c). (Remember, $-pdV = \delta w$.)

8. Computing enthalpy and entropy with a temperature dependent heat capacity.

The heat capacity for liquid *n*-butane depends on temperature:

$$C_p(T) = a + bT,$$

where $a = 100 \text{ J K}^{-1} \text{ mol}^{-1}$ and $b = 0.1067 \text{ J K}^{-2} \text{ mol}^{-1}$, from its freezing temperature $T_f \approx 140 \text{ K}$ to $T_b \approx 270 \text{ K}$, its boiling temperature.

- (a) Compute ΔH for heating liquid butane from $T_A = 170 \text{ K}$ to $T_B = 270 \text{ K}$.
- (b) Compute ΔS for the same process.

- (a) Compute ΔH for heating liquid butane from $T_1 = 170 \text{ K}$ to $T_2 = 270 \text{ K}$.

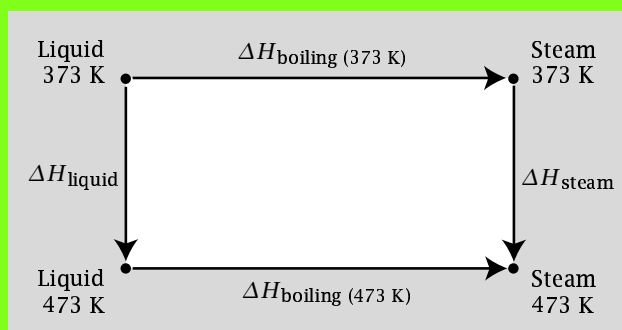
$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} C_p dT = \int_{170}^{270} a dT + \int_{170}^{270} bT dT \\ &= a\Delta T + \frac{bT^2}{2} \Big|_{T_1}^{T_2} = a(270\text{K} - 170\text{K}) + \frac{b}{2} [(270\text{K})^2 - (170\text{K})^2] \\ &= 10.0 \frac{\text{kJ}}{\text{mol}} + 2.35 \frac{\text{kJ}}{\text{mol}} \\ &= 12.35 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

- (b) Compute ΔS for the same process.

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} \frac{C_p}{T} dT = \int_{T_1}^{T_2} \left(\frac{a}{T} + b \right) dT \\ &= a \ln \left(\frac{T_2}{T_1} \right) + b\Delta T \\ &= \left(100 \frac{\text{J}}{\text{K mol}} \right) \ln \left(\frac{270\text{K}}{170\text{K}} \right) + \left(0.1067 \frac{\text{J}}{\text{K}^2 \text{mol}} \right) (100\text{K}) \\ &= 56.93 \frac{\text{J}}{\text{K mol}}\end{aligned}$$

9. Cycle for determining the enthalpy of vaporization of water at 473 K.

Suppose that you want to know how much heat it would take to boil water at 473 K, rather than 373 K. At $T = 373\text{ K}$, $\Delta H_{\text{boiling}(100^\circ\text{C})} = 40.7\text{ kJ mol}^{-1}$ is the enthalpy of vaporization. Assuming that the heat capacities of the liquid ($C_{p,\text{liquid}} = 75\text{ J K}^{-1}\text{mol}^{-1}$) and the vapor ($C_{p,\text{vapor}} = 3.5\text{ J K}^{-1}\text{mol}^{-1}$) are constant over this temperature range, calculate the enthalpy of vaporization at 473 K using the thermodynamic cycle shown in the figure below.



A thermodynamic cycle for calculating the enthalpy of boiling water at a temperature higher than the boiling point.

$$\Delta H_{\text{liquid}} + \Delta H_{373\text{K}} = \Delta H_{473\text{K}} + \Delta H_{\text{steam}}$$

$$\Delta H_{373\text{K}} = 40.7\text{ kJ/mol}$$

$$\begin{aligned}\Delta H_{\text{liquid}} &= \int_{373}^{473} C_{p,\text{liquid}} dT = C_{p,\text{liquid}}(T_2 - T_1) \\ &= (75\text{ J/K mol})(100\text{ K}) = 7.5\text{ kJ/mol}\end{aligned}$$

$$\Delta H_{\text{steam}} = \int_{373}^{473} C_{p,\text{steam}} dT = (3.5\text{ J/K mol})(100\text{ K}) = .35\text{ kJ/mol}$$

$$\Delta H_{473\text{K}} = (40.7\text{ kJ/mol}) + (.35\text{ kJ/mol}) - (7.5\text{ kJ/mol}) = 33.55\text{ kJ/mol}.$$

10. Heating a house.

If your living room, having a volume of $6\text{ m} \times 6\text{ m} \times 3\text{ m} \approx 100\text{ m}^3$, were perfectly insulated, how much energy would be needed to raise the temperature inside the room from $T_{\text{initial}} = 0^\circ\text{C}$ to $T_{\text{final}} = 25^\circ\text{C}$? Note that $C_V = C_p - nR$ for an ideal gas.

Assuming constant heat capacity over the temperature range, the energy required to heat the room is given by

$$(8.a) \quad \Delta U = C_V(T_{\text{final}} - T_{\text{initial}}).$$

To get the heat capacity of the air in the room, assume a mixture of O_2 and N_2 . For an ideal gas, $C_V = C_p - Nk$ and is constant over the given temperature range for both gasses. Table 8-2 gives $C_p = 7\text{ cal/mol deg}$ for either gas, so $C_V = 7\text{ cal/mol deg} - 2\text{ cal/mol deg} = 5\text{ cal/mol deg}$. If we assume the room was sealed at $T = 300\text{ K}$ at 1 atm , the number of moles of gas in the room can be estimated from the ideal gas law,

$$\begin{aligned} n &= \frac{PV}{RT} = \frac{(1\text{ atm})(100\text{ m}^3)}{\left(8.2 \times 10^{-2} \frac{\text{L atm}}{\text{K mol}}\right) \left(\frac{1000\text{ cm}^3}{1\text{ l}}\right) \left(\frac{1\text{ m}}{100\text{ cm}}\right)^3 (300\text{ K})} \\ &= 4067\text{ moles.} \end{aligned}$$

So Equation (8.a) gives

$$\Delta U = \left(\frac{5\text{ cal}}{\text{mol K}}\right) (4065\text{ mol})(25\text{ K}) = 508\text{ kcal}$$

11. Objects in thermal contact.

Suppose two objects A and B , with heat capacities C_A and C_B and initial temperatures T_A and T_B , are brought into thermal contact. If $C_A \gg C_B$, is the equilibrium temperature T closer to T_A or to T_B ?

Use Equation 8.43:

$$T = \frac{C_A T_A + C_B T_B}{C_A + C_B}.$$

Divide the numerator and denominator by C_B to get

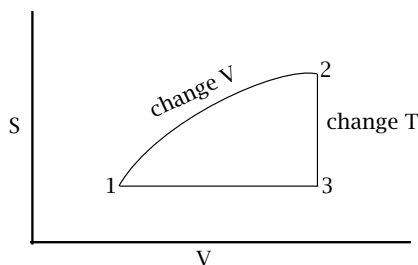
$$T = \frac{\left(\frac{C_A}{C_B}\right) T_A + T_B}{\frac{C_A}{C_B} + 1} \longrightarrow T_A \quad \text{if} \quad \frac{C_A}{C_B} \gg 1.$$

12. ΔS for an adiabatic expansion of a gas.

In an adiabatic quasi-static expansion of an ideal gas, how do you reconcile the following two facts: (1) the increase in volume should lead to an increase in entropy, but (2) in an adiabatic process, $\delta q = 0$ so there should be no change in entropy (since $dS = \delta q/T = 0$)?

Adiabatic expansion of a gas involves both an increase in volume, which increases the entropy, and a decrease in temperature, which decreases the entropy. To show this more quantitatively, consider the total entropy change as a volume increase at constant T and then a temperature change at constant V :

$$S_3 - S_1 = \int dS = \int \frac{\delta q}{T} = 0 = \int \left[\left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT \right]$$



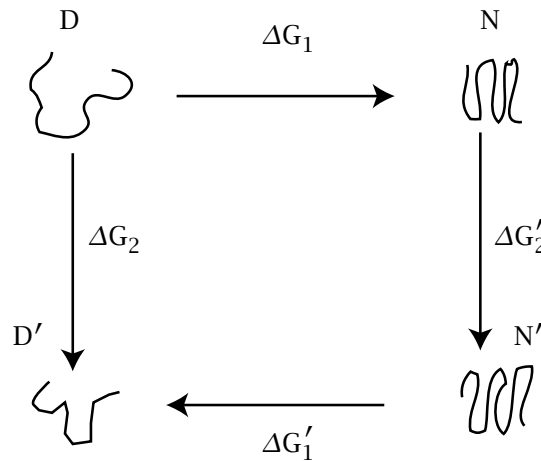
The two terms in the integral are

$$\begin{aligned} \int_1^2 \left(\frac{\partial S}{\partial V} \right)_T dV &= \int \left(\frac{Nk}{V} \right) dV = Nk \ln \left(\frac{V_2}{V_1} \right) = Nk \ln \left(\frac{V_3}{V_1} \right) \text{ since } V_3 = V_2. \\ \int_2^3 \left(\frac{\partial S}{\partial T} \right)_V dT &= \int \left(\frac{C_v dT}{T} \right) = C_v \ln \left(\frac{T_3}{T_2} \right) = C_v \ln \left(\frac{T_3}{T_1} \right) \text{ since } T_1 = T_2. \end{aligned}$$

But according to Equation (8.48), these terms must exactly cancel in a quasi-static adiabatic expansion.

13. A thermodynamic cycle for mutations in protein folding.

Suppose that you can measure the stability of a wild-type protein, $\Delta G_1 = G_{\text{folded}} - G_{\text{unfolded}}$, the free energy difference between folded and unfolded states. A mutant of that protein has a single amino acid replacement. Design a thermodynamic cycle that will help you find the free energy difference $\Delta G_2 = G_{\text{unfolded, mutant}} - G_{\text{unfolded, wildtype}}$, the effect of the mutation on the unfolded state.



From this thermodynamic cycle, with the arrows in the directions indicated,

$$\Delta G_1 + \Delta G'_2 = \Delta G'_1 + \Delta G_2$$

so

$$\Delta G_2 = \Delta G_1 - \Delta G'_1 + \Delta G'_2.$$

You can measure ΔG_1 and $\Delta G'_1$. If you can determine or estimate $\Delta G'_2$, then you can use the above equation to get ΔG_2 . Such estimates are sometimes made by computer simulations.

14. Free energy of an ideal gas.

- (a) For an ideal gas, calculate $F(V)$, the free energy versus volume, at constant temperature.
- (b) Compute $G(V)$.

$$(a) \quad dF = -SdT - pdV + \sum_{i=1}^t \mu_i dN_i = -pdV$$

for constant T and N_i 's. So

$$F(V) = - \int pdV = - \int \frac{NkT}{V} dV = -NkT \ln(V)$$

$$(b) \quad G = H - TS = (U + pV) - TS = (U - TS) + pV = F + pV$$

So

$$G(V) = F(V) + pV = -NkT \ln(V) + NkT = -NkT(\ln(V) - 1)$$

15. Heat capacity of an ideal gas.

The energy of an ideal gas does not depend on volume,

$$\left(\frac{\partial U}{\partial V} \right) = 0.$$

Use this fact to prove that the heat capacities $C_p = (\partial H / \partial T)_p$ and $C_v = (\partial U / \partial T)_V$ for an ideal gas are both independent of volume.

- (a) Use

$$\frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V}$$

and the definition $C_V = (\partial U / \partial T)_V$ to get

$$\frac{\partial C_V}{\partial V} = \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right) = 0,$$

and $(\partial U / \partial V) = 0$, which proves that C_v does not depend on volume V .

$$(b) \quad C_p = \frac{\partial H}{\partial T} = \frac{\partial(U + pV)}{\partial T} = \frac{\partial U}{\partial T} + \frac{\partial(pV)}{\partial T} = \frac{\partial U}{\partial T} + \frac{\partial}{\partial T}(nRT) = \frac{\partial U}{\partial T} + nR.$$

We proved in (a) that $\partial U / \partial T = C_V$ is independent of V , and so is nR , so the last equatino shows that Cp is also independent of V .

16. Computing Entropies.

The heat capacity of an ideal gas is $C_v = \frac{3}{2}Nk$ for N molecules. Assume $T = 300K$ where needed.

- (a) One mole of O_2 gas fills a room of $500m^3$. What is the entropy change, ΔS , for squeezing the gas into $1cm^3$ in the corner of the room?
- (b) An adult takes in about 3000 kcal/day from food (1 food cal = 1 kcal). What is ΔS for this process?
- (c) One mole of O_2 gas is in a room of $500m^3$. What is the entropy change, ΔS , for heating the room from $T = 270K$ to $330K$?
- (d) The free energy of a conformational motion of a loop in a protein is $\Delta G = 2$ kcal/mol. The enthalpy change is $\Delta H = 0.5$ kcal/mol. Compute ΔS .

$$(a) \quad \Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$n = 1 \text{ mole}, R = 2 \text{ cal}/(\text{mol} \cdot K), \frac{V_1}{V_2} = \frac{500m^3}{1cm^3} \left(\frac{100cm}{m}\right)^3$$

$$\frac{V_2}{V_1} = 2.0 \cdot 10^{-9}$$

$$\implies \Delta S = (2 \frac{\text{cal}}{\text{mol} \cdot K}) \ln(2 \cdot 10^{-9}) = -40 \frac{\text{cal}}{\text{mol} \cdot K}$$

(At $T = 300K$, this is equivalent to a free energy of $\Delta F = -T\Delta S \approx 12 \frac{\text{kcal}}{\text{mol}}$)

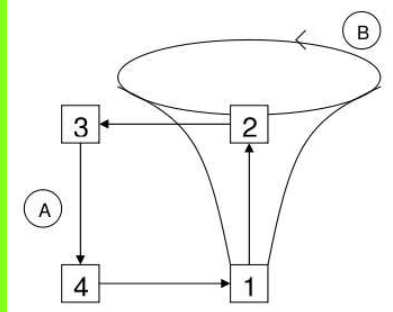
$$(b) \quad \Delta S = \frac{\partial q}{T} = \frac{3000 \text{ kcal}}{300K} = 10 \frac{\text{kcal}}{\text{mol} \cdot K}$$

$$(c) \quad \Delta S = \int_{T_1}^{T_2} \frac{C_v}{T} dT = C_v \ln\left(\frac{T_2}{T_1}\right) = \frac{3}{2} k \ln\left(\frac{330}{270}\right) = 0.6 \frac{\text{cal}}{\text{mol} \cdot K}$$

$$(d) \quad \Delta G = \Delta H - T\Delta S \\ \implies \Delta S = \frac{\Delta H - \Delta G}{T} = \frac{500 - 2000}{300} = -5 \frac{\text{cal}}{\text{mol} \cdot K}$$

17. What powers a hurricane?

A hurricane is powered by a Hadley cycle (A) of rising hot air and falling cold air, coupled to the earth's Coriolis forces (B) that cause the wind circulation.



The reason a hurricane is so strong is that its Hadley cycle is augmented by an additional ingredient, the vaporization of warm water. You can saturate 1 kg of air with 20 grams of water vapor. (You can consider air as consisting of N_2 gas.)

- If air's density is $1.25 \frac{kg}{m^3}$, how many grams of water vapor will occupy $1 m^3$ of air?
- If the enthalpy of vaporization of water is $2.3 \cdot 10^6$ Joules/(kg of water), how much heat, q , is given off by the water when its vapor condenses into rain, per m^3 of air?
- If that heat q , that is given off by water's condensation, all goes into raising the temperature of the surrounding air (at $p=1atm$), what would be the temperature increase, ΔT ?

$$(a) \left(\frac{20g \text{ water}}{kg \text{ air}} \right) \left(\frac{1.25kg \text{ air}}{m^3 \text{ air}} \right) = \frac{25g \text{ water}}{m^3 \text{ air}}$$

$$\frac{20g \text{ water}}{kg \text{ air}}$$

$$(b) \left(\frac{2.3 \cdot 10^6 J}{kg \text{ water}} \right) \left(\frac{1kg}{1000g} \right) \left(\frac{25g \text{ water}}{m^3 \text{ air}} \right) = \frac{5.75 \cdot 10^4 J}{m^3 \text{ air}}$$

$$(c) q = C_p \Delta T$$

$$C_p = \left(7 \frac{cal}{mol} \right) (40.6 moles) \text{ for } N_2 \text{ or } O_2$$

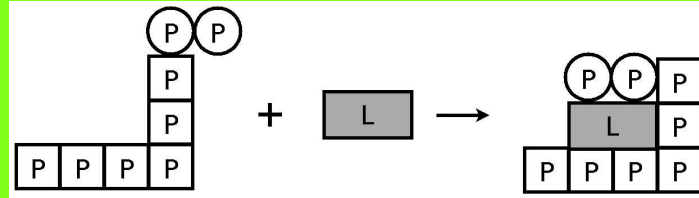
$$\Delta T = \left(\frac{5.75 \cdot 10^4 J}{7 \frac{cal}{mol}} \right) \left(\frac{1cal}{4.2J} \right) \left(\frac{1}{40.6 moles} \right)$$

$$\Rightarrow \Delta T = 48 \text{ degrees}$$

This extra heating drives the density lower, which contributes additional force to the Hadley cycle.

18. Lattice model of ligand binding to a protein.

You have a ligand L and a protein P . When the ligand binds, the energy change is favorable by $5\epsilon_0$ ($\epsilon_0 < 0$) because it makes 5 contacts with the protein. As (crudely) drawn below, the protein is modeled as a simple two-dimensional lattice and consists of a rigid portion (squares containing a 'P') with a flexible loop (circles containing a 'P') at one end. The ligand (rectangle containing an 'L') is rigid and occupies two lattice sites.



- Counting only lateral contacts (no diagonal connections), find the number of conformers, W , of the flexible loop.
- What are the energetic and entropic contributions to the free energy change due to ligand binding? Write an expression for $\Delta F_{\text{binding}}$.
- For $T = 300 \text{ K}$, what is $\Delta F_{\text{binding}} = F_{\text{bound}} - F_{\text{unbound}}$ if $\epsilon_0 = -1 \text{ kcal/mol}$?
- What is the dissociation temperature, T_{dissoc} ?
- If the flexible loop were made rigid instead (and in the proper configuration for ligand binding), what would be the new $\Delta F_{\text{binding}}$?
- Does the ligand bind more tightly or more weakly with the rigid loop?

(a) Since we're only counting lateral contacts, there are 3 possible locations of the first flexible link, and each of these has 3 possible locations for the second flexible link. So, the number of conformers is $W = 9$.

(b) The Helmholtz free energy can be calculated by summing together the energetic term (favorable) and the entropic term (unfavorable, due to the loss of conformer multiplicity):

$$F = U - TS,$$

$$\Delta U = 5\epsilon_0; \quad -T\Delta S = -T \cdot k \ln 9,$$

$$\Delta F_{\text{binding}} = 5\epsilon_0 + kT \ln 9.$$

(c) Plugging values into the expression found in part (b):

$$\begin{aligned}\Delta F_{\text{binding}} &= 5 \cdot (-1 \text{ kcal/mol}) + (0.002 \text{ kcal}/(\text{mol} \cdot \text{K}))(300 \text{ K}) \cdot \ln 9 \\ &= -3.7 \text{ kcal/mol}.\end{aligned}$$

(d) At the dissociation temperature, the free energy change is zero, so:

$$T_{\text{dissoc}} = \frac{|5\epsilon_0|}{k \ln 9} = 1138 \text{ K}.$$

(e)

$$\Delta F_{\text{binding,rigid}} = -5 \text{ kcal/mol}.$$

(f) If the loop is rigid, then the binding will be tighter because it does not incur the entropic penalty from the loss of the loop's conformational freedom. So the free energy is more negative in the rigid case.

Chapter 9

Maxwell's Relations and Mixtures

1. How do thermodynamic properties depend on surface area?

The surface tension of water is observed to decrease linearly with temperature (in experiments at constant p and a): $\gamma(T) = b - cT$, where T = temperature° C, $b = 75.6 \text{ erg cm}^{-2}$ (the surface tension at 0° C) and $c = 0.1670 \text{ erg cm}^{-2}\text{deg}^{-1}$.

- (a) If γ is defined by $dU = TdS - pdV + \gamma da$, where da is the area change of a pure material, give γ in terms of a derivative of the Gibbs free energy at constant T and p .
- (b) Using a Maxwell relation, determine the quantitative value of $(\partial S/\partial a)_{p,T}$ from the relationships above.
- (c) Estimate the entropy change ΔS from the results above if the area of the water/air interface increases by 4 \AA^2 (about the size of a water molecule).

- (a) Since $G = H - TS = U + pV - TS$, we have

$$\begin{aligned} dG &= dU + pdV + Vdp - TdS - SdT \\ &= -SdT + Vdp + \gamma da \end{aligned}$$

so

$$\gamma = \left(\frac{\partial G}{\partial a} \right)_{T,p}$$

$$(b) \quad \left(\frac{\partial S}{\partial a} \right)_{p,T} = - \left(\frac{\partial \gamma}{\partial T} \right)_{p,a} = c = +0.167 \frac{\text{erg}}{\text{cm}^2 \text{ deg}}$$

- (c) Estimate the entropy change ΔS from the results above if the area of the water/air interface increases by 4 \AA^2 , about the size of a water molecule.

$$\begin{aligned}\Delta S &\approx \left(\frac{\partial S}{\partial a}\right) \Delta a \\ &= \left(+0.167 \frac{\text{erg}}{\text{cm}^2 \text{ deg}}\right) \left(\frac{4 \text{ \AA}^2}{\text{molec}}\right) \left(\frac{1 \text{ cm}}{10^8 \text{ \AA}}\right)^2 \\ &\quad \times \left(\frac{1 \text{ cal}}{4.18 \times 10^7 \text{ ergs}}\right) \left(\frac{6.02 \times 10^{23} \text{ molec}}{\text{mole}}\right) \\ \Delta S &= +0.96 \frac{\text{cal}}{\text{mol deg}}\end{aligned}$$

2. Water differs from simple liquids?

Figures 9.5 and 9.6 show that the thermal expansion coefficient $\alpha = (1/V)(\partial V/\partial T)_p$ and isothermal compressibility $\kappa = -(1/V)(\partial V/\partial p)_T$ are both much smaller for water, which is hydrogen-bonded, than for simpler liquids like benzene, which are not. Give a physical explanation for what this implies about molecular packing and entropies in water versus simple liquids.

The observation most directly implies that the volume of water doesn't change as much as other liquids with temperature and pressure. Using the Maxwell relations, it implies the entropy doesn't change as much with pressure as for other liquids. Other liquids are more readily "squeezed" into smaller volume, losing translational entropy, but water isn't so readily squeezed because of its hydrogen bond network.

3. The heat capacity of an ideal gas.

For an ideal gas $(\partial U/\partial V)_T = 0$. Show that this implies the heat capacity C_V of an ideal gas is independent of volume.

Since $U(T, V)$ is a state function,

$$\left(\frac{\partial^2 U}{\partial T \partial V}\right) = \left(\frac{\partial^2 U}{\partial V \partial T}\right),$$

so we have

$$\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right) = 0 \implies \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right) = \frac{\partial C_V}{\partial V} = 0$$

which shows that C_V is independent of V .

4. Using Maxwell relations.

Show that $(\partial H / \partial p)_T = V - T(\partial V / \partial T)_p$.

Start with $dH = TdS + Vdp$.

Now divide by dp , holding T constant:

$$\frac{dH}{dp} \quad [\text{at constant } T] = \left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial S}{\partial p} \right)_T + V.$$

Use the Maxwell relation (Table 9.1),

$$\left(\frac{\partial S}{\partial p} \right)_T = -(\partial V / \partial T)_p$$

to get the result

$$\left(\frac{\partial H}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p + V.$$

5. Pressure dependence of the heat capacity.

(a) Show that, in general, for quasi-static processes

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p.$$

(b) Show that $(\partial C_p / \partial p)_T = 0$ for an ideal gas.

(a) Begin with the definition of the heat capacity,

$$C_p = \frac{\delta q}{dT} = T \frac{dS}{dT}$$

for a quasi-static process. Take the derivative

$$(a) \quad \left(\frac{\partial C_p}{\partial p}\right)_T = T \left(\frac{\partial^2 S}{\partial p \partial T}\right) = T \left(\frac{\partial^2 S}{\partial T \partial p}\right)$$

since S is a state function. Substitute the Maxwell relation

$$\left(\frac{\partial S}{\partial p}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_p$$

into Equation (a) to get

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p.$$

(b) For an ideal gas $V(T) = (NkT)/p$, so

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk}{p} \quad \text{and}$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_p = 0$$

6. Relating G to μ .

Prove that $G = \sum_{i=1}^N \mu_i N_i$.

Substitute Equation (9.29)

$$U = TS - pV + \sum_{i=1}^M \mu_i N_i$$

into $G = H - TS = U + pV - TS$ to get

$$G = \sum_{i=1}^M \mu_i N_i.$$

7. Piezoelectricity.

Apply a mechanical force f along the x -axis of a piezoelectric crystal, such as quartz, which has dimension ℓ in that direction. The crystal will develop a polarization p_0 , a separation of charge along the x -axis, positive on one face and negative on the other. Applying an electric field E along the x -axis causes a mechanical deformation. Such devices are used in microphones, speakers, and pressure transducers. For such systems the energy equation is $dU = TdS + fd\ell + Edp_0$. Find a Maxwell relation to determine $(\partial p_0 / \partial f)_{T,E}$.

You can't use the energy equation to get cross-terms to find $(\partial p_0 / \partial f)_{T,E}$ because $E = (\partial U / \partial p_0)_{S,\ell}$ and $f = (\partial U / \partial \ell)_{S,p_0}$ are derivatives for constant entropy, not constant temperature. So first you need to start with a fundamental function of T , not S . Using Legendre transforms, construct the function $G(T, E, f)$, which is called the piezoelectric Gibbs function,

$$G = U - (TS + f\ell + Ep_0).$$

Substituting dU gives

$$\begin{aligned} dG &= TdS + fd\ell + Edp_0 - TdS - SdT - f d\ell - \ell df - Edp_0 - p_0 dE \\ &= -SdT - \ell df - p_0 dE. \end{aligned}$$

Taking cross-derivatives gives

$$\left(\frac{\partial \ell}{\partial E}\right)_{T,f} = \left(\frac{\partial p_0}{\partial f}\right)_{T,E}.$$

$(\partial \ell / \partial E)$ requires a measurement of how the length of the crystal changes with the applied field E .

8. Relating C_V and C_p .

Show that $C_p = C_V + Nk$ for an ideal gas.

There are various ways to do this. One way is to recognize that

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad \text{and} \quad C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

so you can start with the equation $S(T, p)$,

$$(a) \quad dS = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp.$$

For constant volume, divide Equation (a) by dT and multiply by T

$$\begin{aligned} T \left(\frac{\partial S}{\partial T} \right)_V &= T \left(\frac{\partial S}{\partial T} \right)_p + T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V \\ (b) \quad \implies C_V &= C_p + T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V. \end{aligned}$$

Substitute the Maxwell relation

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$$

into Equation (b) to get

$$(c) \quad C_V = C_p - T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_V.$$

For an ideal gas, $pV = NkT$, so

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{Nk}{p} \quad \text{and} \quad \left(\frac{\partial p}{\partial T} \right)_V = \frac{Nk}{V}.$$

Substituting these expressions into Equation (e) gives

$$C_V = C_p - \left(\frac{NkT}{p} \right) \left(\frac{Nk}{V} \right) = C_p - Nk.$$

9. Rubber bands are entropic springs.

Experiments show that the retractive force f of polymeric elastomers as a function of temperature T and expansion L is approximately given by $f(T, L) = aT(L - L_0)$ where a and L_0 are constants.

- (a) Use Maxwell relations to determine the entropy and enthalpy, $S(L)$ and $H(L)$, at constant T and p .
- (b) If you adiabatically stretch a rubber band by a small amount its temperature increases, but its volume does not change. Derive an expression for its temperature T as a function of L , L_0 , a , and its heat capacity $C = (\partial U / \partial T)$.

- (a) To use the Maxwell relation, Equation (9.12), we take the derivative of the equation of state to get

$$\left(\frac{\partial f}{\partial T} \right)_{p,L} = a(L - L_0).$$

Using Equation (9.18) gives

$$\left(\frac{\partial S}{\partial L} \right)_{T,p} = -a(L - L_0).$$

Integrating gives

$$S(L) = \frac{-a(L - L_0)^2}{2}$$

which shows that the entropy follows a square-law, like a Hooke's law spring. For $H(L)$, use Equation (9.20):

$$\left(\frac{\partial H}{\partial L}\right)_{T,p} = f - T \left(\frac{\partial f}{\partial T}\right)_{L,p} = aT(L - L_0) - aT(L - L_0) = 0.$$

(b) For an adiabatic process, the derivation parallels that of Example 8.8:

$$dU = \delta q + \delta w = f dL$$

since $\delta q = 0$ and the pV work component is zero. Also $dU = C_V dT$, so

$$\begin{aligned} C_V dT &= aT(L - L_0) dL \\ \Rightarrow \int_{T_1}^{T_2} \frac{C_V}{T} dT &= \int_{L_0}^L a(L - L_0) dL \\ \Rightarrow C_V \ln\left(\frac{T_2}{T_1}\right) &= \frac{a(L - L_0)^2}{2} \\ \Rightarrow \frac{T_2}{T_1} &= \exp\left[\frac{a(L - L_0)^2}{2C_V}\right] \end{aligned}$$

10. Metal elasticity is due to energy, not entropy.

Experiments show that the retractive force f of metal rods as a function of temperature T and extension L relative to undeformed length L_0 is given by $f(T, L) = Ea\Delta L/L_0$, where $\Delta L = L[1 - \alpha(T - T_0)] - L_0 = L - L\alpha(T - T_0) - L_0$. a is the cross-sectional area of the rod, E (which has the role of a spring constant) is called *Young's modulus*, and $\alpha \approx 10^{-5}$ is the linear expansion coefficient. Compute $H(L)$ and $S(L)$. Is the main dependence on L due to enthalpy H or entropy S ?

To get the enthalpy, use Table 8.1:

$$dH = TdS + Vdp + f dL = C_p dT + \frac{Ea(L - L_0)}{L_0} dL.$$

Integrating gives

$$H(L) = C_p(T - T_0) + \frac{Ea}{2L_0}(L - L_0)^2.$$

To get the entropy, use

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T} \right)_L dT + \left(\frac{\partial S}{\partial L} \right)_T dL \\ &= \frac{C_L}{T} dT - \left(\frac{\partial f}{\partial T} \right)_L dL \end{aligned}$$

where C_L is the heat capacity of a rod held at constant length, and we have used Maxwell's relation Equation (9.19). Since

$$\left(\frac{\partial f}{\partial T} \right)_L = -\frac{EaL\alpha}{L_0},$$

equation (a) becomes

$$dS = \frac{C_L}{T} dT + \frac{Ea\alpha L}{L_0} dL$$

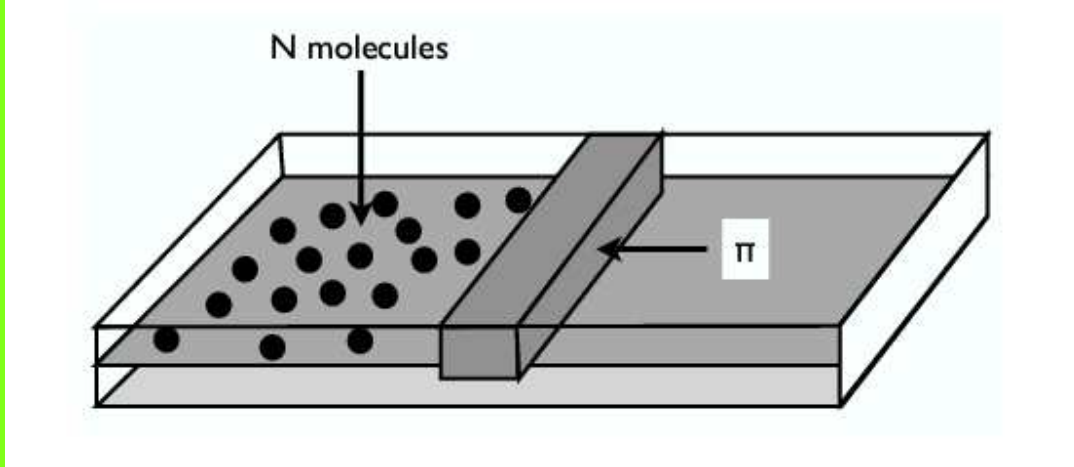
and integrating gives

$$S(T, L) = \int_{T_0}^T \frac{C_L(T)}{T} dT + \frac{Ea\alpha L^2}{2L_0} + \text{constant}.$$

Since $\alpha = 10^{-5}$ appears in $S(L)$ but not in $H(L)$, the dominant L dependence is in the enthalpy for metals. For polymers, stretching mostly affects the entropy.

11. Pressures in Surfactant Monolayers

A Langmuir trough is shown below. N surfactant molecules float on water on the left side of a bar. When you push the bar to the left with pressure π , the N surfactant molecules occupy an equilibrium area A , where



$$\pi = -\left(\frac{\partial G}{\partial A}\right)_{T,P,N}$$

Consider a 2-dimensional van der Waals model in which the entropy is given by

$$S = k \ln(A - A_0)$$

where A_0 is the minimum area the molecules can occupy when they crowd together, and the enthalpy by

$$H = -\frac{b}{a}$$

- (a) You can express the pressure in terms of components: enthalpic (π_H) and entropic (π_S):

$$\pi = \pi_H + \pi_S$$

Write a Maxwell's relation for

$$\pi_S = T\left(\frac{\partial S}{\partial A}\right)_{T,P,N}$$

- (b) Express π_H in terms of measurable quantities, T and A .
(c) Write the "equation of state" of the model, which is the quantity $\pi(N, A, T)$.
(d) Write an expression for the free energy $\Delta G(N, T, A)$ at constant p .

(a) $dG = -SdT + VdP + \mu dN - \pi dA$

$$\begin{aligned}\frac{\partial G}{\partial T} &= -S, \frac{\partial G}{\partial P} = V, \frac{\partial G}{\partial N} = \mu, \frac{\partial G}{\partial A} = -\pi \\ \frac{\partial^2 G}{\partial T \partial A} &= \frac{\partial^2 G}{\partial A \partial T} \implies -\frac{\partial \pi}{\partial T} = -\frac{\partial S}{\partial A} \\ \frac{\partial S}{\partial A} &= \frac{\partial \pi}{\partial T} \\ \implies \pi_S &= T \frac{\partial \pi}{\partial T}\end{aligned}$$

(b) $G = H - TS \implies \frac{\partial G}{\partial A} = \frac{\partial H}{\partial A} - T \frac{\partial S}{\partial A} - S \frac{\partial T}{\partial A}$
 At constant T and for $\pi = -\frac{\partial G}{\partial A}$, $-\frac{\partial G}{\partial A} = T \frac{\partial S}{\partial A} - \frac{\partial H}{\partial A}$
 $\pi = \pi_S + \pi_H \implies \pi_H = -\frac{\partial H}{\partial A}$

$$\begin{aligned}\pi_H &= \pi - \pi_S \\ \pi_H &= \pi - T \frac{\partial \pi}{\partial T}\end{aligned}$$

OR

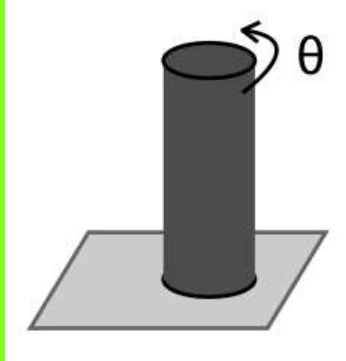
$$H = -\frac{B}{A} \implies \frac{\partial H}{\partial A} = \frac{B}{A^2} \implies \pi_H = -\frac{\partial H}{\partial A} = -\frac{B}{A^2}$$

(c) $\pi = T \frac{\partial S}{\partial A} - \frac{\partial H}{\partial A}$
 $S = k \ln(A - A_0) \implies \frac{\partial S}{\partial A} = \frac{k}{A - A_0}$
 $H = -\frac{B}{A} \implies \frac{\partial H}{\partial A} = \frac{B}{A^2}$
 $\pi = \frac{kT}{A - A_0} - \frac{B}{A^2}$

(d) $\pi = -\frac{\partial G}{\partial A} = \frac{kT}{A - A_0} - \frac{B}{A^2} \implies$
 $\Delta G = -\int \frac{kT}{A - A_0} - \frac{B}{A^2} dA$
 $\Delta G = [-kT \ln(A - A_0) - \frac{B}{A}]_{A_1}^{A_2}$
 $\Delta G = [-kT \ln(A_2 - A_0) - \frac{B}{A_2}] + [kT \ln(A_1 - A_0) + \frac{B}{A_1}]$
 $\Delta G = kT \ln(\frac{A_1 - A_0}{A_2 - A_0}) + \frac{B}{A_1} - \frac{B}{A_2}$
 $\Delta G = kT \ln(\frac{A_1 - A_0}{A_2 - A_0}) + \frac{B(A_2 - A_1)}{A_1 A_2}$

12. Torque on DNA.

One end of a DNA molecule is fixed to a surface. Using single-molecule methods, a torque (twisting force) is applied to the other end, to twist the molecule.



When the molecule is twisted through an angle θ , the DNA gives a restoring torque τ that depends on temperature T ,

$$\tau = (k_0 + k_1 T)\theta$$

where k_0 and k_1 are measured constants.

- Write an expression for the free energy $G(\theta)$ at fixed T and p .
- Use a Maxwell relation to express $(\frac{\partial S}{\partial \theta})_{T,p}$ in terms of experimental observables, where S is entropy and p is pressure.
- Derive an expression for $S(\theta)$, at constant T and p .
- Derive an expression for the enthalpy, $H(\theta)$, at constant T and p .
- Under what conditions, i.e. for what values of k_0 , k_1 , and T , will this torsional retractive force be entropy-driven?

$$\begin{aligned} \text{(a)} \quad & \tau = (k_0 + k_1 T)\theta \\ & dG = -SdT + Vdp + \mu dN + \tau d\theta \\ & \implies \tau = \left(\frac{\partial G}{\partial \theta}\right)_{T,p,N} \implies G(T, \theta) = \int \tau d\theta \\ & \implies G(T, \theta) = \frac{1}{2}(k_0 + k_1 T)\theta^2 \end{aligned}$$

$$\text{(b)} \quad \text{From the equation for } dG \text{ above, the Maxwell relation is:} \\ \left(\frac{\partial S}{\partial \theta}\right)_{T,p,N} = -\left(\frac{\partial \tau}{\partial T}\right)_{\theta,p,N}$$

$$\text{(c)} \quad \text{Since } \left(\frac{\partial \tau}{\partial T}\right)_{\theta,p,N} = k_1\theta = -\frac{\partial S}{\partial \theta}, \text{ you have} \\ S(\theta) = -\int k_1\theta d\theta = -\frac{k_1}{2}\theta^2$$

(d) Since $\tau = \frac{\partial G}{\partial \theta} = \frac{\partial H}{\partial \theta} - T \frac{\partial S}{\partial \theta}$, rearranging gives

$$\frac{\partial H}{\partial \theta} = \tau + T \frac{\partial S}{\partial \theta} = (k_0 + k_1 T) \theta - k_1 T \theta = k_0 \theta$$

$$\implies H(\theta) = \int k_0 \theta d\theta = \frac{k_0 \theta^2}{2}$$

(e) If k_0 is more negative than $k_1 T$, the torque is entropy-driven.

13. The Massieu Function: $J(\beta, V, N)$.

Whereas the entropy is an extremum function $S(U, V, N)$, it is sometimes useful to use a related extremum function, $J(\beta, V, N)$ where $\beta = 1/T$ and T is temperature. For this function, β and U are conjugate variables.

- (a) Derive an expression for the differential quantity dJ in terms of variations $d\beta$, dV , and dN . (Hint: as an initial guess for J , try either $J = S + \beta U$ or $J = S - \beta U$).
- (b) Using additional reduced variables $\pi = p/T$ and $m = \mu/T$, write Maxwell relations for:

$$\begin{aligned} \left(\frac{\partial \pi}{\partial N}\right)_{\beta, V} &= \\ \left(\frac{\partial U}{\partial V}\right)_{\beta, N} &= \\ \left(\frac{\partial U}{\partial N}\right)_{\beta, V} &= \end{aligned}$$

- (c) What is the relation between J and the Helmholtz free energy $F(T, V, N)$?

- (a) Let $J = S - \beta U$, then

$$\begin{aligned} dJ &= dS - \beta dU - U d\beta = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN - \beta dU - U d\beta \\ \implies dJ &= -U d\beta + p \beta dV + \mu \beta dN \end{aligned}$$

- (b) In reduced quantities,

$$dJ = -\mu d\beta + \pi dV - m dN$$

So the Maxwell's relations, which are just the cross-derivatives are

$$\begin{aligned} \left(\frac{\partial \pi}{\partial N}\right)_{\beta, V} &= -\frac{\partial m}{\partial V} \\ \left(\frac{\partial U}{\partial V}\right)_{\beta, N} &= -\frac{\partial \pi}{\partial \beta} \\ \left(\frac{\partial U}{\partial N}\right)_{\beta, V} &= \frac{\partial m}{\partial \beta} \end{aligned}$$

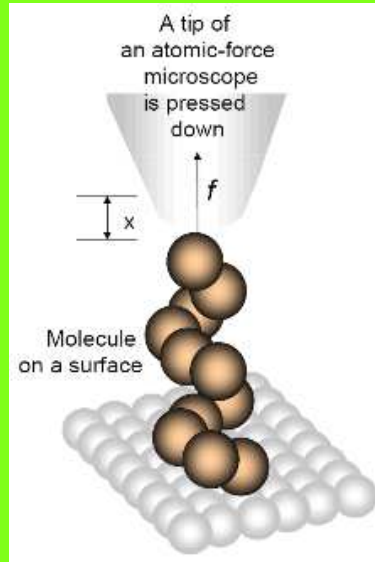
- (c) Multiply the equation, $J = S - \beta U$, by $(-T)$ to get

$$\begin{aligned} -JT &= -TS + T\beta U = U - TS = F \\ \implies J &= -\beta F \end{aligned}$$

The utility of the Massieu function comes from the relationship that $\frac{F}{kT} = -\ln K$, so $J \sim \ln K$ is proportional to the experimentally observable equilibrium constant.

14. Thermodynamics of a single molecule.

One end of a molecule is fixed to a surface. Another end is pressed down by the tip of an atomic force microscope.



Using the tip of an atomic force microscope as a probe, we measure the force of molecule retraction. The force depends on the temperature at which the experiment is performed as follows

$$f = (aT + b)x, \text{ where } a \text{ and } b \text{ are constants}$$

- Produce a fundamental equation describing the energy of the molecule. Write an expression for dG at fixed T , P . Derive an expression showing how G depends on x .
- Use a Maxwell relation to express $(\frac{\partial S}{\partial x})_{T,P}$.
- Derive an expression for $S(x)$, at fixed T , P .
- Derive an expression for enthalpy $H(x)$ at fixed T , P .
- What values of a and b will produce a condition that the retraction force is driven by a change in entropy?

$$\begin{aligned} \text{(a)} \quad dU &= TdS + PdV + \mu dN + Fdx \\ dG &= -SdT + VdP + Fdx \\ F &= (\frac{\partial G}{\partial x})_{T,P} \\ G(x) &= \int (aT + b)x dx = \frac{1}{2}(aT + b)x^2 \end{aligned}$$

- (b) $(\frac{\partial S}{\partial x})_{T,P} = -(\frac{\partial F}{\partial T})_{x,P}$
- (c) $(\frac{\partial S}{\partial x})_{T,P} = -(\frac{\partial F}{\partial T})_{x,P} = -ax$
 $S(x) = \int -ax dx = -\frac{1}{2}ax^2$
- (d) $F = (\frac{\partial G}{\partial x})_{T,P} = (\frac{\partial H}{\partial x})_{T,P} - T(\frac{\partial S}{\partial x})_{T,P} = (\frac{\partial H}{\partial x})_{T,P} + T(\frac{\partial F}{\partial T})_{x,P}$
 $(\frac{\partial H}{\partial x})_{T,P} = F + T(\frac{\partial S}{\partial x})_{T,P} = (aT + b)x + T(-ax) = aTx + bx - Tax = bx$
 $\implies H(x) = \int bx dx = \frac{1}{2}bx^2$
- (e) Entropy of the molecule has to decrease when x decreases (we press on the molecule).
 Thus, the coefficient a has to be negative for $a < 0$, and
 $(\frac{\partial H}{\partial x})_{T,P} << T(\frac{\partial F}{\partial T})_{x,P}$
 $bx << aTx$
 $b << aT < 0$
 b is more negative than aT.

15. Gibbs-Helmholtz Equation.

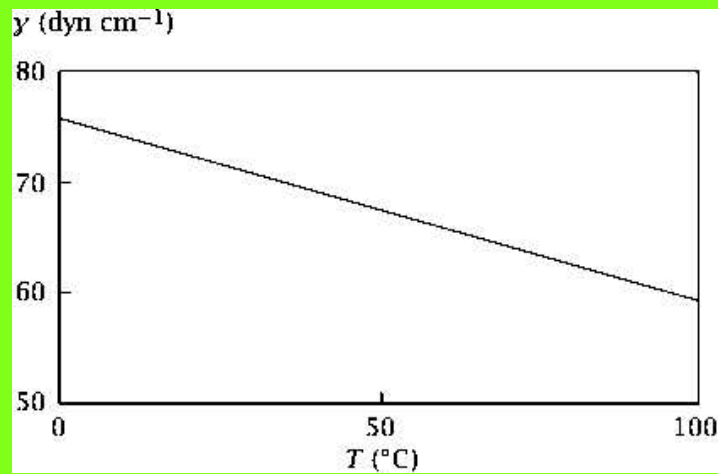
From the definition of $G=H-TS$, derive the Gibbs-Helmholtz equation:

$$\frac{\partial}{\partial T}(\frac{G}{T}) = -\frac{H}{T^2}$$

which relates the temperature variation of the Gibbs free energy G to the enthalpy H.

Starting with $G = H - T(\frac{\partial G}{\partial T})_{p,N}$, and multiplying both sides by $(-\frac{1}{T^2})$
 $-\frac{G}{T^2} - \frac{1}{T}(\frac{\partial G}{\partial T})_{p,N} = -\frac{H}{T^2}$
 $\frac{\partial}{\partial T}(\frac{G}{T}) = -\frac{H}{T^2}$

16. Surface tension components.



The figure shows the surface tension of water as a function of temperature.

- From the figure, determine the numerical value of $\frac{\partial \gamma}{\partial T}_{p,N,a}$, where T = temperature, p = pressure, and a = surface area.
- Find the Maxwell relation for the partial derivative equal to $\frac{\partial \gamma}{\partial T}_{p,N,a}$.
- Write an expression for the enthalpic and entropic components of the surface tension γ .
- Combining the results from above, compute the numerical values of the enthalpic and entropic parts of γ at $T = 300$ K, and comment on which component dominates the surface tension.

- From the slope:

$$\frac{\partial \gamma}{\partial T} = -0.15 \frac{\text{dyn}}{\text{cm} \cdot \text{deg}}.$$

- Use Eq. (9.6) to get the appropriate cross term:

$$\left(\frac{\partial \gamma}{\partial T} \right)_{p,N,a} = - \left(\frac{\partial S}{\partial a} \right)$$

(c)

$$\gamma = \left(\frac{\partial G}{\partial a} \right)_{T,p,N} = \left(\frac{\partial H}{\partial a} \right)_{T,p,N} - T \left(\frac{\partial S}{\partial a} \right)_{T,p,N}.$$

(See Eq. (9.14) for an equivalent problem.)

(d)

$$\text{Entropic part} = -T \frac{\partial S}{\partial a} = T \frac{\partial \gamma}{\partial T} = -0.15 \frac{\text{dyn}}{\text{cm} \cdot \text{deg}} \cdot 300 \text{ K}$$

$$= 45 \text{ dyn/cm}.$$

(e) At $T = 300 \text{ K}$, $\gamma \approx 70 \text{ dyn/cm}$, so the enthalpic part is:

$$\frac{\partial H}{\partial a} = \gamma - T \frac{\partial \gamma}{\partial T} = 70 - 45 = 25 \text{ dyn/cm}.$$

Therefore water's surface tension is dominated by entropy. This is because water is a structured liquid.

17. Exploring the quantity F/T .

Sometimes a quantity of interest is the Helmholtz Free Energy $F(T, V, N)$ divided by T . (For example, this quantity is proportional to the logarithms of equilibrium constants or solubilities.)

- (a) Derive a relationship showing that

$$\frac{\partial(F/T)}{\partial T} \propto U.$$

Find the constant of proportionality.

- (b) Suppose $F(T)$ depends on temperature in the following way: $F(T) = 2aT^2 + bT$ (so $F/T = 2aT + b$). Find $S(T)$ and $U(T)$.
- (c) For this and the next parts of this problem, consider a transition between a helix and coil state of a polymer. F/T is related to the ratio of populations as $F/T = -k \ln(K_{eq})$, where $K_{eq} = N_{coil}/N_{helix}$. Using $F/T = 2aT + b$ from above, at what temperature are the helix and coil in equilibrium (*e.g.*, half of the molecules are helical and half are unfolded).
- (d) Assuming $a > 0$, does increasing the temperature favor the helix or the coil?

- (a) There are several ways to solve this problem. Consider a couple of them:

$$\begin{aligned} \frac{F}{T} &= \frac{U}{T} - S \\ \frac{\partial}{\partial T} \left(\frac{U}{T} - S \right) &= \frac{\partial U}{\partial T} \cdot \frac{1}{T} - \frac{U}{T^2} - \frac{\partial S}{\partial T} \\ &= \frac{\partial U}{\partial S} \cdot \frac{\partial S}{\partial T} \cdot \frac{1}{T} - \frac{U}{T^2} - \frac{\partial S}{\partial T} \\ &= T \cdot \frac{\partial S}{\partial T} \cdot \frac{1}{T} - \frac{U}{T^2} - \frac{\partial S}{\partial T} \\ &= \frac{\partial S}{\partial T} - \frac{U}{T^2} - \frac{\partial S}{\partial T} \\ \implies \frac{\partial(F/T)}{\partial T} &= -\frac{U}{T^2} \end{aligned}$$

OR

$$\begin{aligned} \frac{\partial(F/T)}{\partial T} &= \frac{1}{T} \cdot \frac{\partial F}{\partial T} - \frac{F}{T^2} \\ &= \frac{1}{T}(-S) - \frac{U-TS}{T^2} \\ &= -\frac{S}{T} - \frac{U}{T^2} + \frac{S}{T} \\ \implies \frac{\partial(F/T)}{\partial T} &= -\frac{U}{T^2} \end{aligned}$$

- (b) $\frac{\partial F}{\partial T} = -S(T) = -(4aT + b)$
 $\implies S(T) = 4aT + b$
 $F = U + TS$
 $2aT^2 + bT = U(T) + 4aT^2 + bT$
 $\implies U(T) = -2aT^2$

- (c) $\frac{F}{T} = -k \ln(K_{eq})$
 $\frac{2aT+b}{1/2} = -k \ln(1/2)$

$$2aT + b = 0$$

$$\implies T = -\frac{b}{2a}$$

- (d) $\frac{\partial(F/T)}{\partial T} = 2a$, for $a > 0$ is always positive. Thus,
 $\frac{\partial(k \ln(K_{eq}))}{\partial T} < 0$
 and this favors a coil.

Chapter 10

The Boltzmann Distribution Law

1. The statistical thermodynamics of a cooperative system.

Perhaps the simplest statistical mechanical system having ‘cooperativity’ is the three-level system in the following table.

Energies	$2\varepsilon_0$	ε_0	0
Degeneracies	γ	1	1

- Write an expression for the partition function q as a function of energy ε , degeneracy γ , and temperature T .
- Write an expression for the average energy $\langle \varepsilon \rangle$ versus T .
- For $\varepsilon_0/kT = 1$ and $\gamma = 1$, compute the populations, or probabilities, p_1^* , p_2^* , p_3^* of the three levels.
- Now if $\varepsilon_0 = 2 \text{ kcal mol}^{-1}$ and $\gamma = 1000$, find the temperature T_0 at which $p_1 = p_3$.
- Under condition (d), compute p_1^* , p_2^* , and p_3^* at temperature T_0 .

$$(a) \quad q = 1 + e^{-\varepsilon_0/kT} + \gamma e^{-2\varepsilon_0/kT}$$

$$(b) \quad \begin{aligned} \langle \varepsilon_0 \rangle &= 0p_0 + \varepsilon_0 p_1 + 2\varepsilon_0 p_2 \\ &= \frac{1}{q} \left[\varepsilon_0 e^{-\varepsilon_0/kT} + 2\varepsilon_0 \gamma e^{-2\varepsilon_0/kT} \right] = -\frac{\partial \ln q}{\partial \beta} \end{aligned}$$

$$(c) \quad q = 1 + e^{-1} + e^{-2} = 1.5032$$

$$p_1 = \frac{1}{q} = 0.6652$$

$$p_2 = \frac{e^{-1}}{q} = 0.2447$$

$$p_3 = \frac{e^{-2}}{q} = 0.0900$$

$$(d) \quad \text{Since } p_1 = 1/q \text{ and } p_3 = \gamma e^{-2\varepsilon_0/kT}/q, \text{ we want}$$

$$\gamma e^{-2\varepsilon_0/kT_0} = 1 \implies -\frac{2\varepsilon_0}{kT_0} = \ln(1/\gamma) = -6.9078$$

$$\implies T_0 = \frac{2(2000 \text{ cal/mol})}{6.9078(2 \text{ cal/mol})} = 289.5 \text{ K}$$

(Use R in place of k for molar calculations)

$$(e) \quad \frac{\varepsilon_0}{kT} = \frac{2000 \text{ cal/mol}}{(2 \text{ cal/(mol deg)})(289.5 \text{ deg})} = 3.4539$$

$$\text{Now } q = 1 + e^{-3.45} + 1000e^{-6.9078} = 2.0317$$

$$p_1 = \frac{1}{q} = 0.4922 = p_3$$

$$p_2 = e^{-3.45}/q = 0.0156$$

2. Speed of sound.

The speed of sound in air is approximately the average velocity $\langle v_x^2 \rangle^{1/2}$ of the gas molecules. Compute this speed for $T = 0^\circ \text{ C}$, assuming that air is mostly nitrogen gas.

An equation on p. 183 gives

$$\langle v_x^2 \rangle^{1/2} = \left(\frac{kT}{m} \right)^{1/2} = \left(\frac{RT}{M} \right)^{1/2}$$

where R is the gas constant and $M = 28 \text{ gm/mol}$ is the molecular weight. We have

$$\langle v_x^2 \rangle^{1/2} = \left[\frac{\left(8.314 \frac{\text{J}}{\text{Kmol}} \right) (273\text{K})}{0.028 \text{ kg/mol}} \right]^{1/2} = 285 \frac{\text{m}}{\text{sec}}.$$

The actual speed of sound in air is 346 ms^{-1} at 300 K.

3. Properties of a two-state system.

Given a two-state system in which the low energy level is 600 cal mol^{-1} , the high energy level is $1800 \text{ cal mol}^{-1}$, and the temperature of the system is 300 K,

(a) What is the partition function q ?

(b) What is the average energy $\langle \varepsilon \rangle$?

$$(a) \quad q = 1 + e^{-(\varepsilon_2 - \varepsilon_1)/kT} = 1 + e^{-1200/(2)(300)} = 1 + e^{-2} = 1.135$$

$$\begin{aligned} (b) \quad \langle \varepsilon \rangle &= \varepsilon_1 p_1 + \varepsilon_2 p_2 \\ &= 600 \frac{\text{cal}}{\text{mol}} \left(\frac{1}{q} \right) + 1800 \frac{\text{cal}}{\text{mol}} \left(\frac{e^{-2}}{q} \right) \\ &= 600 \frac{\text{cal}}{\text{mol}} \left(\frac{1 + 3e^{-2}}{1 + e^{-2}} \right) = 743 \frac{\text{cal}}{\text{mol}} \end{aligned}$$

4. Binding to a surface.

Consider a particle that has two states: bonded to a surface, or non-bonded (released). The non-bonded state is higher in energy by an amount ε_0 .

- (a) Explain how the ability of the particle to bond to the surface contributes to the heat capacity, and why the heat capacity depends on temperature.
- (b) Compute the heat capacity C_V in units of Nk if $T = 300\text{ K}$ and $\varepsilon_0 = 1.2\text{ kcal mol}^{-1}$ (which is about the strength of a weak hydrogen bond in water).

(a) This binding process adds an energy ladder (in this case it has only two states) to whatever energy levels exist. This provides an energy storage mechanism, thus a heat capacity (since $C_V = \partial U / \partial T$). This heat capacity depends on temperature because equipartition does not apply to a two-state system. At low temperatures, only the lowest level is populated (all particles are bonded) and small increments of thermal energy cannot be stored as excitations. At high temperatures, only the highest level is populated (all particles are unbound and free) and no further energy storage is possible. Only at intermediate temperatures can the system absorb energy by releasing bound molecules.

(b) Using the Schottky two-state model,

$$\frac{C_V}{Nk} = \left(\frac{\varepsilon}{kT} \right)^2 \frac{e^{-\varepsilon/kT}}{(1 + e^{-\varepsilon/kT})^2}.$$

$$\frac{\varepsilon}{kT} = \frac{1.2 \times 10^3 \frac{\text{cal}}{\text{mol}}}{1.987 \frac{\text{cal}}{\text{molK}} 300\text{K}} = 2.013 \implies -e^{\varepsilon/kT} = 0.134, \quad \text{so}$$

$$\frac{C_V}{Nk} = (2.013)^2 \frac{0.134}{(1 + 0.134)^2} = 0.421.$$

5. Entropy depends on distinguishability

Given a system of molecules at $T = 300 \text{ K}$, $q = 1 \times 10^{30}$, and $\Delta U = 3740 \text{ J mol}^{-1}$,

- (a) What is the molar entropy if the molecules are distinguishable?
- (b) What is the molar entropy if the molecules are indistinguishable?

- (a) For *distinguishable* particles, where $Q = q^N$, the molar entropy is

$$\begin{aligned}\frac{S}{n} &= R \ln q + \frac{\Delta U}{nT} \\ \frac{\Delta U}{n} &= 3740 \text{ J/mol} \implies \frac{S}{n} = \left(8.314 \frac{\text{J}}{\text{mol K}}\right) \ln(10^{30}) + \frac{(3740 \text{ J})}{300 \text{ mol K}} \\ \implies \frac{S}{n} &= 586.8 \frac{\text{J}}{\text{K mol}}\end{aligned}$$

- (b) For *indistinguishable* particles, $Q = \frac{q^N}{N!} \approx \frac{q^N}{(\frac{N}{e})^N} \implies \ln Q \approx N \ln q - N(\ln N - 1)$, so

$$\frac{S}{n} = R[\ln q - \ln N + 1] + \frac{\Delta U}{nT}$$

$N = n\mathcal{N}_A$ where N = no. of molecules,
 n = no. of moles and \mathcal{N}_A = Avogadro's number.

$$\begin{aligned}\implies \frac{S}{n} &= R \ln \left(\frac{q}{n\mathcal{N}_A} + 1 \right) + \frac{\Delta U}{nT} \\ &= \left(8.31 \frac{\text{J}}{\text{molK}} \right) \left[\ln \left(\frac{10^{30}}{6 \times 10^{23}} \right) + 1 \right] + \frac{3740}{300} = 139.9 \frac{\text{J}}{\text{molK}}\end{aligned}$$

Note that S is larger if particles are distinguishable.

6. The Boltzmann distribution of uniformly-spaced energy levels.

A system has energy levels uniformly spaced at 3.2×10^{-20} J apart. The populations of the energy levels are given by the Boltzmann distribution. What fraction of particles is in the ground state at $T = 300$ K?

The energies of this system are $0, \varepsilon, 2\varepsilon, \dots$, where $\varepsilon = 3.2 \times 10^{-20}$ J. Then

$$q = \sum_{i=0}^{\infty} e^{-i\varepsilon/kT},$$

which is a geometric series of the form

$$\sum_{k=0}^{\infty} ax^k$$

with $a=1$, and $x = e^{-\varepsilon/kT} < 1$. Using Equation (4.4), we get

$$q = \frac{1}{1 - e^{-\varepsilon/kT}} = \frac{1}{1 - e^{-7.72}} = 1.0004.$$

So $p_0^* = \frac{1}{q} = 1 - e^{-7.72} = 0.9996$ —only 0.04% of the molecules are *not* in the ground state.

7. The population of spins in a magnetic field.

The nucleus of a hydrogen atom, a proton, has a magnetic moment. In a magnetic field, the proton has two states of different energy; spin up and spin down. This is the basis of proton NMR. The relative populations can be assumed to be given by the Boltzmann distribution, where the difference in energy between the two states is $\Delta\varepsilon = g\mu B$, $g = 2.79$ for protons, and $\mu = 5.05 \times 10^{-24}$ J Tesla⁻¹. For a 300 MHz NMR instrument, $B = 7$ Tesla.

- (a) Compute the relative population difference, $|N_+ - N_-|/(N_+ + N_-)$, at room temperature for a 300 MHz machine.
- (b) Describe how the population difference changes with temperature.
- (c) What is the partition function?

$$\begin{aligned}
\text{(a)} \quad \frac{N_{\uparrow}}{N_{\downarrow}} &= e^{\frac{\varepsilon}{kT}} \implies N_{\uparrow} = N_{\downarrow} e^{\frac{\varepsilon}{kT}} \\
\implies N_{\uparrow} + N_{\downarrow} &= N_{\downarrow} (1 + e^{\frac{\varepsilon}{kT}}) \\
N_{\uparrow} - N_{\downarrow} &= N_{\downarrow} (e^{\frac{\varepsilon}{kT}} - 1) \\
\frac{|N_{\uparrow} - N_{\downarrow}|}{N_{\uparrow} + N_{\downarrow}} &= \frac{1 - e^{-\frac{\varepsilon}{kT}}}{1 + e^{\frac{\varepsilon}{kT}}}.
\end{aligned}$$

For small $\frac{\varepsilon}{kT}$, $1 - e^{-\frac{\varepsilon}{kT}} \approx \frac{\varepsilon}{kT}$, so

$$\begin{aligned}
\frac{|N_{\uparrow} - N_{\downarrow}|}{N_{\uparrow} + N_{\downarrow}} &\approx \frac{\frac{\varepsilon}{kT}}{2 - \frac{\varepsilon}{kT}} \approx \frac{\varepsilon}{2kT} \\
&= \frac{(2.79)(5.05 \times 10^{-24} \text{ J/Tesla})(7 \text{ Tesla})}{2(300K)(1.38 \times 10^{-23} \text{ J/K})} \\
&= 1.19 \times 10^{-2}
\end{aligned}$$

This is the fractional population difference.

(b) As T increases, the population *difference* decreases (populations become equal). As $T \rightarrow 0$, all of the population goes to the lower energy state.

(c) $q = 1 + e^{\frac{\varepsilon}{kT}}$ (if the lower energy state is taken as the ground state, with respect to which the other energy is measured).

8. Energy and entropy for indistinguishable particles.

Equations (10.34) for $\langle \varepsilon \rangle$ and (10.37) for S apply to distinguishable particles. Compute the corresponding quantities for systems of indistinguishable particles.

For indistinguishable particles, $Q = \frac{q^N}{N!} \approx \left(\frac{q}{N}\right)^N$, so

$$\Delta U = - \left(\frac{\partial \ln Q}{\partial \beta} \right) \approx - \frac{\partial}{\partial \beta} (N \ln q - N \ln N + N) = -N \left(\frac{\partial \ln q}{\partial \beta} \right),$$

$$\text{so } \langle \varepsilon \rangle = \frac{\Delta U}{N} = \frac{\Delta U}{N} = - \left(\frac{\partial \ln q}{\partial \beta} \right) \implies \langle \varepsilon \rangle \text{ doesn't depend on distinguishability.}$$

$$\begin{aligned} \text{Now } S &= k \ln Q + \frac{\Delta U}{T} = Nk(\ln q - \ln N + 1) - \frac{N}{T} \left(\frac{\partial \ln q}{\partial \beta} \right) \\ &= S_{\text{distinguishable}} - \ln N + 1 < S_{\text{distinguishable}} \quad \text{for } N > 2 \text{ particles.} \end{aligned}$$

As seen in problem 5, the entropy is larger for distinguishable systems.

9. Computing the Boltzmann distribution.

You have a thermodynamic system with three states. You observe the probabilities $p_1 = 0.9$, $p_2 = 0.09$, $p_3 = 0.01$ at $T = 300 \text{ K}$. What are the energies ε_2 and ε_3 of states 2 and 3 relative to the ground state?

$$\begin{aligned} q &= 1 + e^{-\frac{\varepsilon_2}{kT}} + e^{-\frac{\varepsilon_3}{kT}} \\ p_1 &= \frac{1}{q} = 0.9 \implies q = \frac{10}{9} \\ p_2 &= \frac{e^{-\frac{\varepsilon_2}{kT}}}{q} = 0.9e^{-\frac{\varepsilon_2}{kT}} = 0.09 \implies e^{-\frac{\varepsilon_2}{kT}} = \frac{1}{10} \\ \implies \varepsilon_2 &= kT \ln 10 = \left(2 \frac{\text{cal}}{\text{K mol}} \right) (300\text{K}) \ln 10 = 1.38 \frac{\text{kcal}}{\text{mol}} \\ p_3 &= \frac{e^{-\frac{\varepsilon_3}{kT}}}{q} = 0.9e^{-\frac{\varepsilon_3}{kT}} = 0.01 \implies e^{-\frac{\varepsilon_3}{kT}} = \frac{1}{90} \\ \implies \varepsilon_3 &= kT \ln 90 = \left(2 \frac{\text{cal}}{\text{K mol}} \right) (300\text{K}) \ln 90 = 2.70 \frac{\text{kcal}}{\text{mol}} \end{aligned}$$

10. The pressure reflects how energy levels change with volume.

If energy levels $\varepsilon_i(V)$ depend on the volume of a system, show that the pressure is the average

$$p = -N \left\langle \frac{\partial \varepsilon}{\partial V} \right\rangle.$$

From the fundamental energy equation, $p = - \left(\frac{\partial \Delta U}{\partial V} \right)_{S,N}$. But $\Delta U = N \langle \varepsilon \rangle$ so

$$\begin{aligned} p &= -N \left(\frac{\partial \langle \varepsilon \rangle}{\partial V} \right)_{S,N} = -N \left(\frac{\partial}{\partial V} \sum_1^N \varepsilon_i(V) p_i \right) = -N \left(\sum_1^N \frac{\partial}{\partial V} \varepsilon_i(V) p_i \right) \\ &= -N \left(\sum_1^N \left(\frac{\partial \varepsilon_i(V)}{\partial V} \right) p_i \right) = -N \left\langle \frac{\partial \varepsilon}{\partial V} \right\rangle. \end{aligned}$$

11. End-to-end distance in polymer collapse.

Use the two-dimensional four-bead polymer of Example 10.3. The distance between the chain ends is 1 lattice unit in the compact conformation, 3 lattice units in the extended conformation, and $\sqrt{5}$ lattice units in each of the other three chain conformations. Plot the average end-to-end distance as a function of temperature, if the energy is

(a) $\varepsilon = 1 \text{ kcal mol}^{-1}$.

(b) $\varepsilon = 3 \text{ kcal mol}^{-1}$.

To get the average end-to-end length, $\langle d \rangle$,

use the Boltzmann probabilities p_j for each of the $j = 1, 2, \dots, 5$ conformations:

$$\langle d \rangle = \sum_{j=1}^5 p_j d_j = (1) \left(\frac{1}{q} \right) + \sqrt{5} \left(\frac{3e^{\frac{-\varepsilon}{kT}}}{q} \right) + 3 \left(\frac{e^{\frac{-\varepsilon}{kT}}}{q} \right)$$

where $q = 1 + 4e^{\frac{-\varepsilon}{kT}}$,

so $\langle d \rangle = \frac{1 + 9.71e^{\frac{-\varepsilon}{kT}}}{1 + 4e^{\frac{-\varepsilon}{kT}}}.$

The maximum end-to-end distance ($T \rightarrow \infty$) is

$$\frac{(1 + 3\sqrt{5} + 3)}{5} = 2.14.$$

The midpoint is at $\langle d \rangle = 1.57$. You can find the midpoint temperature T_0 from

$$\begin{aligned} (1.57) \left(1 + 4e^{\frac{-\varepsilon}{kT_0}} \right) &= 1 + 9.71e^{\frac{-\varepsilon}{kT_0}} \\ \Rightarrow \frac{0.57}{3.43} &= e^{\frac{-\varepsilon}{kT_0}}. \end{aligned}$$

$$(a) \quad T_0 = \frac{\left(1000 \frac{\text{cal}}{\text{mol}} \right)}{\left(2 \frac{\text{cal}}{\text{molK}} \right) \ln \left(\frac{3.43}{0.57} \right)} = 278\text{K}$$

$$(b) \quad T_0 = 835\text{K}$$

12. The lattice model of dimerization.

Use the lattice model for monomers bonding to form dimers, and assume large volumes $V \gg 1$.

- (a) Derive the partition function.
- (b) Compute $p_1(T)$ and $p_2(T)$, the probabilities of monomers and dimers as a function of temperature, and sketch the dependence on temperature.
- (c) Compute the bond breakage temperature T_0 at which $p_1 = p_2$.

- (a) If you choose the convention that the ground state (dimer) has zero energy and the dissociated state has energy $\varepsilon > 0$, then the partition function is

$$\begin{aligned} Q &= \sum_{\varepsilon} g(\varepsilon) e^{-\frac{\varepsilon}{kT}} \\ &= (V-1) + \left(\frac{V}{2} - 1 \right) (V-1) e^{-\frac{\varepsilon}{kT}} \end{aligned}$$

(b) The Boltzmann populations are

$$P_{\text{monomer}} = \frac{\left(\frac{V}{2} - 1\right) e^{-\frac{\varepsilon}{kT}}}{1 + \left(\frac{V}{2} - 1\right) e^{-\frac{\varepsilon}{kT}}}$$

$$P_{\text{dimer}} = \frac{1}{1 + \left(\frac{V}{2} - 1\right) e^{-\frac{\varepsilon}{kT}}}$$

(c) The populations are equal when

$$\left(\frac{V}{2} - 1\right) e^{-\frac{\varepsilon}{kT_0}} = 1$$

$$\Rightarrow -\frac{\varepsilon}{kT_0} = -\ln\left(\frac{V}{2} - 1\right)$$

$$\Rightarrow T_0 = \frac{\varepsilon}{k \ln\left(\frac{V}{2} - 1\right)}$$

which is the same result we found in Equation (8.8)

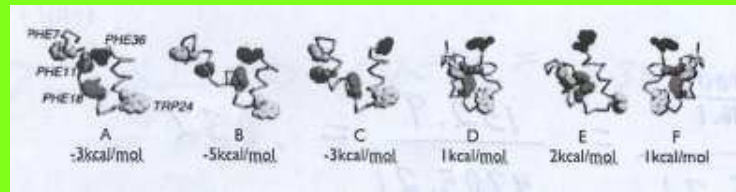
13. Equivalent premises for Boltzmann distribution.

Use Equation (10.6) to show that the distribution of probabilities p_j^* that minimizes the free energy F at constant (T, V, N) is the same distribution that maximizes the entropy S at constant $(U, V, N) = (\langle E \rangle, V, N)$.

It is clear that requiring $dS = 0$, subject to the constraint that $dU = 0$, is the same as requiring $dF = dU - TdS = 0$, if T is constant.

14. Protein conformations.

Assume a protein has six different discrete conformations, with energies given in the figure below.



- Write an expression for the probability, $p(i)$ of finding the protein in conformation i .
- Write an expression for the probability, $p(E)$ of finding the protein having energy E .
- Use the expressions you wrote in (a) and (b) to calculate the following probabilities:
 - $p(\text{State}_B)$.
 - $p(\text{State}_A)$.
 - $p(\text{State}_D)$.
 - $p(1 \text{ kcal/mol})$.
 - $p(-5 \text{ kcal/mol})$.
- What is the average energy of the ensemble of conformations?

$$(a) \quad p(\text{State}_i) = \frac{e^{\frac{-E_{\text{State}_i}}{RT}}}{e^{\frac{3000}{RT}} + e^{\frac{5000}{RT}} + e^{\frac{3000}{RT}} + e^{\frac{-1000}{RT}} + e^{\frac{-2000}{RT}} + e^{\frac{-1000}{RT}}}$$

$$RT = 1.987 \frac{\text{cal}}{\text{K} \cdot \text{mol}} 300\text{K} = 596.1 \frac{\text{cal}}{\text{mol}}$$

$$\Rightarrow Q = e^{5.03} + e^{8.39} + e^{5.03} + e^{-1.68} + e^{-3.36} + e^{-1.68}$$

$$Q = 152.9 + 4399 + 152.9 + 0.19 + 0.03 + 0.19 = 4705.21$$

$$(b) \quad P(E) = \frac{W(E)e^{-\frac{E}{RT}}}{Q}$$

where $Q = 4705.21$

$$W(-3 \frac{\text{kcal}}{\text{mol}}) = 2, W(-5 \frac{\text{kcal}}{\text{mol}}) = 1, W(1 \frac{\text{kcal}}{\text{mol}}) = 2, W(2 \frac{\text{kcal}}{\text{mol}}) = 1$$

$$(c) \quad (a) \quad p(\text{State}_B) = \frac{e^{\frac{5000}{596.1}}}{4705.21} = \frac{4399}{4705.21} = 0.935$$

$$(b) \quad p(\text{State}_A) = \frac{e^{\frac{3000}{596.1}}}{4705.21} = \frac{152.9}{4705.21} = 0.032$$

$$(c) \quad p(\text{State}_D) = \frac{e^{\frac{-1000}{596.1}}}{4705.21} = \frac{0.19}{4705.21} = 4.04 \cdot 10^{-5}$$

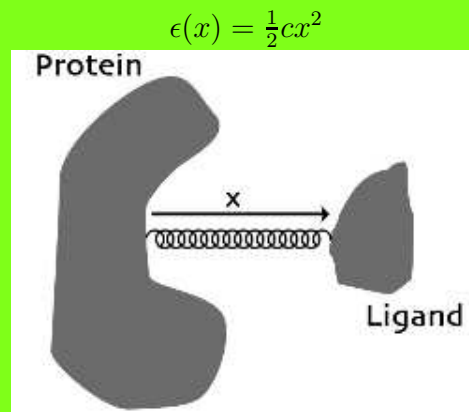
$$(d) \quad p(1 \text{ kcal/mol}) = \frac{2 \cdot e^{\frac{-1000}{596.1}}}{4705.21} = \frac{2 \cdot 0.19}{4705.21} = 8.08 \cdot 10^{-5}$$

$$(e) \quad p(-5 \text{ kcal/mol}) = \frac{1 \cdot e^{\frac{5000}{596.1}}}{4705.21} = \frac{4399}{4705.21} = 0.935$$

$$\begin{aligned}
 \text{(d) } \langle E \rangle &= \sum_i E_i p_i \\
 &= \\
 &= -3000 \cdot 0.032 - 5000 \cdot 0.935 - 3000 \cdot 0.032 + 1000 \cdot 4.04 \cdot 10^{-5} + 2000 \cdot 8.08 \cdot 10^{-5} + 1000 \cdot 4.04 \cdot 10^{-5} \\
 &= -96 - 4675 - 96 + 0.0404 + 0.1616 + 0.0404 = -4866.6 \frac{\text{cal}}{\text{mol}}
 \end{aligned}$$

15. Modeling ligand binding.

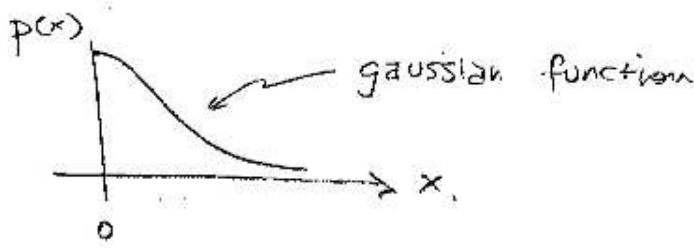
A ligand is bound to a protein with a spring-like square-law energy $\epsilon(x)$, where x is the distance between the ligand and protein as shown in the figure.



- For constant (T, V, N) , write an expression for the probability distribution $p(x)$ of the ligand separation from the protein.
- Sketch a plot of $p(x)$ vs x .
- Write an expression for the average location of the ligand, $\langle x \rangle$.
- Write an expression for the second moment of the location of the ligand, $\langle x^2 \rangle$.
- Calculate the average energy, $\langle \epsilon \rangle$ of the system.

$$\begin{aligned}
 \text{(a) } p(x) &= \frac{e^{-\beta\epsilon(x)}}{Q}, x \geq 0 \\
 p(x) &= \frac{e^{-\frac{cx^2}{2kT}}}{\int_0^\infty e^{-\frac{cx^2}{2kT}} dx} = \sqrt{\frac{2c}{\pi kT}} e^{-\frac{cx^2}{2kT}}
 \end{aligned}$$

- Sketch



$$(c) \langle x \rangle = \frac{\int_0^\infty x p(x) dx}{\int_0^\infty p(x) dx} = \frac{\int_0^\infty x e^{-\frac{cx^2}{2kT}} dx}{\int_0^\infty e^{-\frac{cx^2}{2kT}} dx}$$

Look up these integrals in the appendix D:

$$\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$$

$$\text{Here, } a = \frac{c}{2kT}$$

$$\Rightarrow \langle x \rangle = \left(\frac{1}{2a}\right) \left(2\sqrt{\frac{a}{\pi}}\right) = \frac{1}{\sqrt{\pi a}} = \sqrt{\frac{2kT}{\pi c}}$$

$$(d) \langle x^2 \rangle = \frac{\int_0^\infty x^2 e^{-\frac{cx^2}{2kT}} dx}{\int_0^\infty e^{-\frac{cx^2}{2kT}} dx}$$

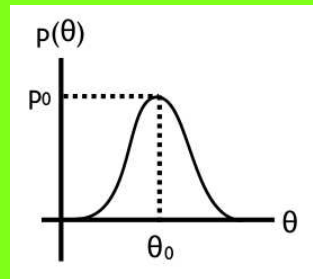
$$= \frac{\frac{1}{4a} \sqrt{\frac{\pi}{a}}}{\frac{1}{2} \sqrt{\frac{\pi}{a}}} = \frac{1}{2a} = \frac{kT}{c}$$

$$(e) \langle \epsilon \rangle = \left\langle \frac{1}{2} cx^2 \right\rangle = \frac{1}{2} c \langle x^2 \rangle = \frac{kT}{2}$$

This is also expected from the equipartition theorem.

16. Distribution of torsional angles.

In a computer simulation that samples a molecular torsion angle θ , you observe a gaussian distribution, $p(\theta)$, shown in the figure below.



$$p(\theta) = p_0 e^{-k_s(\theta - \theta_0)^2}$$

What is the underlying energy function $E(\theta)$ that gives rise to it?

Since the Boltzmann law is: $p(\theta) = p_0 e^{\frac{-E(\theta)}{kT}}$, you have:

$\frac{E(\theta)}{kT} = -\ln\left(\frac{p(\theta)}{p_0}\right) = k_s(\theta - \theta_0)^2$
 This is a spring-like square-law energy.

17. 3-bead polymer chain model.

Consider a 3-bead polymer that can undergo conformational change from a non-linear to a linear form, as shown in Figure A. Both conformations have the same energy. Now suppose the X and Y atoms of the polymer can bind a ligand L (Figure B). Breaking one bond increases the energy by ϵ to breaking two bonds increases the energy by 2ϵ . Assume that the ligand-bound conformation has the lowest energy.

Figure A:

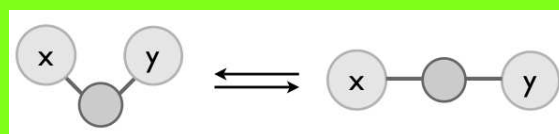
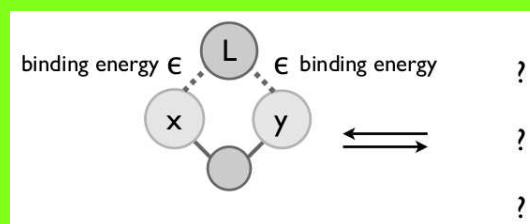
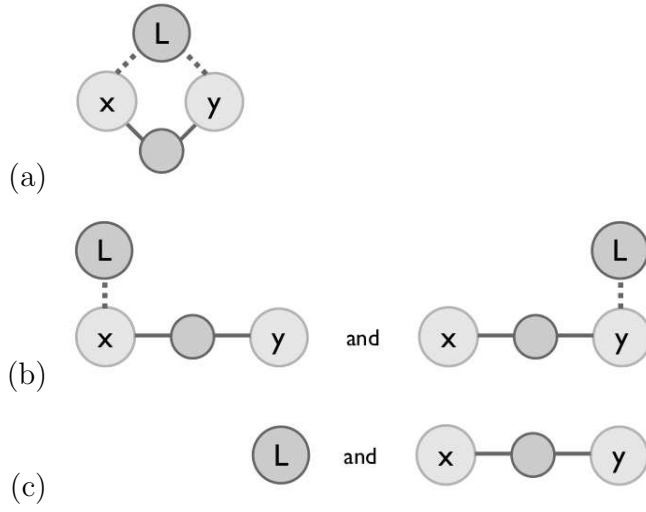


Figure B:



- Draw a picture showing the possible binding states.
- Calculate the equilibrium probabilities of these conformations.
- Plot the population distribution of the conformations at temperature $kT = 0$ and $kT = 1.4\epsilon$. What is the difference in entropy between these two temperatures.
- Plot the distribution at high temperatures ($T \rightarrow \infty$) and explain its shape.
- What is the average energy of the system at each temperature in part (c)?

(a) Possible conformations:



(b) Probabilities:

$$p_1 = \frac{1}{1+2e^{-\epsilon/kT}+e^{-2\epsilon/kT}}$$

$$p_2 = \frac{2e^{-\epsilon/kT}}{1+2e^{-\epsilon/kT}+e^{-2\epsilon/kT}}$$

$$p_3 = \frac{e^{-2\epsilon/kT}}{1+2e^{-\epsilon/kT}+e^{-2\epsilon/kT}}$$

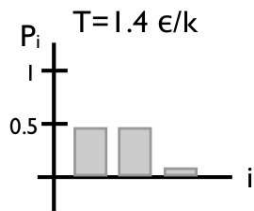
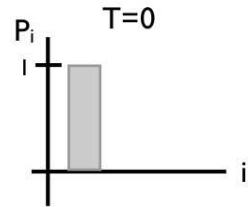
(c) Distributions:

$$p_1 = \frac{1}{1+2e^{-1/1.4}+e^{-2/1.4}} = \frac{1}{1+2e^{-1/1.4}+e^{-2/1.4}} \approx 0.45$$

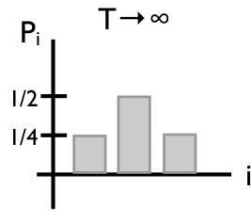
$$p_2 = \frac{2e^{-\epsilon/kT}}{1+2e^{-\epsilon/kT}+e^{-2\epsilon/kT}} \approx 0.44$$

$$p_3 = \frac{e^{-2\epsilon/kT}}{1+2e^{-\epsilon/kT}+e^{-2\epsilon/kT}} \approx 0.11$$

$$S = -k \sum_{i=1}^3 p_i \ln \frac{p_i}{g_i} = k(0.45 \ln 0.45 + 0.44 \ln 0.22 + 0.11 \ln 0.11) \approx 1.27k$$



(d) Partition function at $T \rightarrow \inf$ is $Q = 1 + 2 + 1$



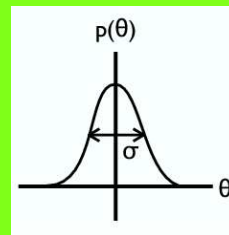
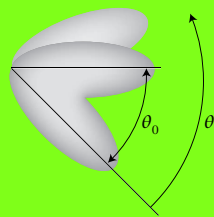
(e) Average energy:

For $T = 0$: $\langle E \rangle = 0$

For $T = 1.4\epsilon/k$: $\langle E \rangle = 0 * 0.45 + 1 * 0.44 + 2 * 0.11 = 0.66$

18. Protein hinge motions.

A protein has two domains, connected by a flexible hinge. The hinge fluctuates around an angle θ_0 . The distribution of the angles is gaussian, around θ_0 , as shown in the second figure below.



$$p(\theta) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(\theta-\theta_0)^2}{2\sigma^2}\right).$$

where σ is the standard deviation.

- Assume a Boltzmann distribution of probabilities: $p(\theta) = b \cdot \exp\left(-\frac{c(\theta-\theta_0)^2}{kT}\right)$, with energy $\epsilon = c(\theta - \theta_0)^2$. Derive the value of b .
- If you measure a standard deviation $\sigma = 30$ deg, what is the value of c ?
- Derive an expression relating $\langle \theta^2 \rangle$ to c . Assume $T = 300$ K.
- Derive an expression for the entropy in terms of kT and c : $\frac{S}{k} = - \int_{-\infty}^{+\infty} p(\theta) \ln(p(\theta)) d\theta$.
- If a mutant of the protein has fluctuations that are smaller than the wild type, $\langle \theta^2 \rangle_M = \frac{1}{2} \langle \theta^2 \rangle_{WT}$, what is the change in entropy, $\Delta S = S_M - S_{WT}$, where S_M is the entropy of the mutant and S_{WT} is the entropy of the original wild-type protein?

(a) We must have $\int_{-\infty}^{\infty} p(\theta) d\theta = 1$,

$$\text{so } \frac{1}{b} = \int_{-\infty}^{\infty} \exp \frac{-c(\theta-\theta_0)^2}{kT} d\theta = \sqrt{\frac{\pi kT}{c}}$$

$$\implies b = \sqrt{\frac{c}{\pi kT}}$$

You can also see this by noticing that

$$2\sigma^2 = \frac{kT}{c}, \text{ so } \sigma = \sqrt{\frac{kT}{2c}}$$

$$b = \frac{1}{\sigma\sqrt{2\pi}} = \sqrt{\frac{c}{\pi kT}}$$

(b) You have $c = \frac{RT}{2\sigma^2} = \frac{600 \frac{\text{cal}}{\text{mol}}}{2(900 \text{deg}^2)} = \frac{1}{3} \frac{\text{cal}}{\text{mol} \cdot \text{deg}^2} = 2.4 \cdot 10^{-24} \frac{J}{\text{deg}^2}$

(c) $\langle (\theta - \theta_0)^2 \rangle = \int_{-\infty}^{\infty} (\theta - \theta_0)^2 \sqrt{\frac{c}{\pi kT}} e^{\frac{-c(\theta-\theta_0)^2}{kT}} d\theta$

Use $\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$ to get

$$\langle (\theta - \theta_0)^2 \rangle = \frac{kT}{2c} = \sigma^2$$

(d) $\frac{S}{k} = - \int_{-\infty}^{\infty} [\sqrt{\frac{c}{\pi kT}} e^{-\frac{c\theta^2}{kT}}] [\ln(\sqrt{\frac{c}{\pi kT}}) - \frac{c\theta^2}{kT}] d\theta$

$$= -\sqrt{\frac{c}{\pi kT}} \ln(\sqrt{\frac{c}{\pi kT}}) \int_{-\infty}^{\infty} e^{-\frac{c\theta^2}{kT}} d\theta + \sqrt{\frac{c}{\pi kT}} \int_{-\infty}^{\infty} (\frac{c\theta^2}{kT}) e^{-\frac{c\theta^2}{kT}} d\theta$$

$$= -\sqrt{\frac{c}{\pi kT}} \ln(\sqrt{\frac{c}{\pi kT}}) \sqrt{\frac{\pi kT}{c}} + \frac{1}{2}$$

$$\frac{S}{k} = -\ln(\sqrt{\frac{c}{\pi kT}}) + \frac{1}{2}$$

(e) $\Delta S = S_m - S_{wt} = -k \ln(\sqrt{\frac{c_m}{c_{wt}}})$

$$= -k \ln(\sqrt{\frac{\langle \theta_{wt}^2 \rangle}{\langle \theta_m^2 \rangle}})$$

$$= -k \ln \sqrt{2}$$

Chapter 11

Statistical Mechanics of Simple Gases and Solids

1. The heat capacity of an ideal gas.

What is the heat capacity C_V of an ideal gas of argon atoms?

$$\begin{aligned}\Delta U &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right) \\ &= \frac{NkT^2}{a} \left(\frac{\partial q}{\partial T} \right) \\ &= \frac{3}{2} NkT \\ C_V &= \frac{\partial \Delta U}{\partial T} = \frac{3}{2} Nk.\end{aligned}$$

2. The statistical mechanics of oxygen gas.

Consider a system of one mole of O_2 molecules in the gas phase at $T = 273.15 \text{ K}$ in a volume $V = 22.4 \times 10^{-3} \text{ m}^3$. The molecular weight of oxygen is 32.

- (a) Calculate the translational partition function $q_{\text{translation}}$.
- (b) What is the translational component of the internal energy per mole?
- (c) Calculate the constant-volume heat capacity.

$$\begin{aligned}
\text{(a)} \quad q_{\text{translation}} &= \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V \\
m &\approx 32 \frac{\text{gm}}{\text{mol}} = 5.31 \times 10^{-26} \frac{\text{kg}}{\text{molecule}} \\
k &= 1.38 \times 10^{-23} \text{ JK}^{-1} \\
T &= 273.15 \text{ K} \\
h &= 6.626 \times 10^{-34} \text{ J s} \\
q_{\text{translation}} &= \left[\frac{(6.28)(5.32 \times 10^{-26} \text{ kg})(3.77 \times 10^{-21} \text{ J})}{(6.63 \times 10^{-34} \text{ J s})^2} \right]^{3/2} (22.4 \times 10^{-3} \text{ m}^3) \\
&= 3.43 \times 10^{30} \frac{\text{accessible states}}{\text{molecule}} \quad \left(\text{note : } \frac{\text{kg m}^2}{\text{s}^2} = \text{J} \right)
\end{aligned}$$

$$\text{(b)} \quad \Delta U_{\text{translation}} = \frac{3}{2} RT (\text{per mole}) = 3.4 \frac{\text{kJ}}{\text{mole}}$$

$$\text{(c)} \quad C_V (\text{per mole}) = \left(\frac{\partial \Delta U}{\partial T} \right)_V = \frac{3}{2} R = 12.47 \frac{\text{J}}{\text{Kmol}}$$

3. The statistical mechanics of a basketball.

Consider a basketball of mass $m = 1 \text{ kg}$ in a basketball hoop. To simplify, suppose the hoop is a cubic box of volume $V = 1 \text{ m}^3$.

- (a) Calculate the lowest two energy states using the particle-in-a-box approach.
- (b) Calculate the partition function at $T = 300 \text{ K}$. Show whether quantum effects are important or not. (Assume that they are important only if q is smaller than about 10.)

(a) Three-dimensional particle-in-a-box

$$\varepsilon = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

two lowest energy states:

1. $n_x = n_y = n_z = 1$ $(n_x^2 + n_y^2 + n_z^2) = 3$
2. 2 n 's = 1 and 1 $n = 2$, $(1^2 + 1^2 + 2^2) = 6$, so

$$\begin{aligned}\varepsilon_1 &= \frac{3h^2}{8mL^2} & \varepsilon_2 &= \frac{6h^2}{8mL^2} \\ \frac{h^2}{mL^2} &= \frac{(6.63 \times 10^{-34} \text{ J s})^2}{(1\text{kg})(1 \text{ m})^2} = 4.39 \times 10^{-67} \text{ J} \\ \varepsilon_1 &= 1.65 \times 10^{-67} \\ \varepsilon_2 &= 3.30 \times 10^{-67} \text{ J}\end{aligned}$$

$$\begin{aligned}\text{(b)} \quad q_{\text{translation}} &= \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \\ &= \left[\frac{(6.28)(1 \text{ kg})(1.38 \times 10^{-23} \text{ J/K})(300 \text{ K})}{(6.63 \times 10^{-34} \text{ J s})^2} \right]^{3/2} (1/\text{m})^3 \\ &= 1.44 \times 10^{70} \frac{\text{accessible states}}{\text{molecule}}\end{aligned}$$

Quantum effects are clearly not important for objects as large as basketballs.

4. The statistical mechanics of an electron.

Calculate the two lowest energy levels for an electron in a box of volume $V = 1 \text{ \AA}^3$ (This is an approximate model for the hydrogen atom). Calculate the partition function at $T = 300 \text{ K}$. Are quantum effects important?

(a) As above

$$\varepsilon_1 = \left(\frac{3h^2}{8mL^2} \right), \quad \varepsilon_2 = \frac{3h^2}{4mL^2}$$

where m = mass of the electron = 9.11×10^{-31} kg

$$\frac{h^2}{mL^2} = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{(9.11 \times 10^{-31} \text{ kg})(10^{-10} \text{ m})^2} = 4.82 \times 10^{-17} \text{ J}$$

$$\varepsilon_1 = 1.81 \times 10^{-17} \text{ J}$$

$$\varepsilon_2 = 3.62 \times 10^{-17} \text{ J}$$

$$\begin{aligned} \text{(b)} \quad q_{\text{translation}} &= \left[\frac{(6.28)(9.11 \times 10^{-31} \text{ kg})(4.14 \times 10^{-21} \text{ J})}{(6.63 \times 10^{-34} \text{ J s})^2} \right]^{3/2} (10^{-10} \text{ m})^3 \\ &= 1.25 \times 10^{-5}; \end{aligned}$$

The classical approximation is *not* valid (since $q < 10$), and quantum effects are important. Since q cannot be smaller than 1, the value obtained above is an artifact of the assumption that the sum in the partition function can be approximated as an integral for this problem.

5. The translational partition function in two dimensions.

When molecules adsorb on a two-dimensional surface, they have one less degree of freedom than in three dimensions. Write the two-dimensional translational partition function for an otherwise structureless particle.

For each dimension

$$q_{\text{translation,1D}} = \left[\frac{2\pi mkT}{h^2} \right]^{1/2} L$$

and $q_{\text{translation,2D}} = q_{\text{translation,1D}}^2$ so if $A = \text{area} = L^2$, then

$$q_{\text{translation,2D}} = \left(\frac{2\pi mkT}{h^2} \right) A$$

6. The accessibility of rotational degrees of freedom.

Diatomic ideal gases at $T = 300$ K have rotational partition functions of approximately $q = 200$. At what temperature would q become small (say $q < 10$) so that quantum effects become important?

$$q_{\text{rot}} = \frac{8\pi^2 I k T}{\sigma h^2}$$

If $q_{\text{rot}} = 200$ at $T = 300$ K, then

$$\frac{8\pi^2 I k}{\sigma h^2} = \frac{2}{3}. \quad q_{\text{rot}} = \frac{2}{3} T = 10,$$

about when quantum effects become important, when $T = 15$ K.

7. The statistical thermodynamics of harmonic oscillations.

Write the internal energy, entropy, enthalpy, free energy, and pressure for a system of N independent distinguishable harmonic oscillators.

For harmonic oscillators, $q = \frac{e^{-h\nu\beta}}{1 - e^{-h\nu\beta}}$. For distinguishable particles, $Q = q^N$.

$$(a) \quad \frac{\Delta U}{N} = -\frac{1}{q} \frac{\partial q}{\partial \beta} = \frac{h\nu e^{-h\nu\beta}}{1 - e^{-h\nu\beta}}$$

$$(b) \quad \begin{aligned} \frac{S}{kN} &= \ln q + \frac{\Delta U}{NkT} \\ \frac{S}{kN} &= -\ln(1 - e^{-h\nu\beta}) + \left(\frac{h\nu}{kT}\right) \left(\frac{e^{-h\nu\beta}}{1 - e^{-h\nu\beta}}\right) \end{aligned}$$

$$(c) \quad F = -kT \ln Q \implies \frac{F}{NkT} = -\ln q = +\ln(1 - e^{-h\nu\beta}).$$

(Alternatively $F = \Delta U - TS$, and the result in (c) is obtained directly from (a) and (b).)

$$(d) \quad p = - \left(\frac{\partial F}{\partial V} \right)_T = 0$$

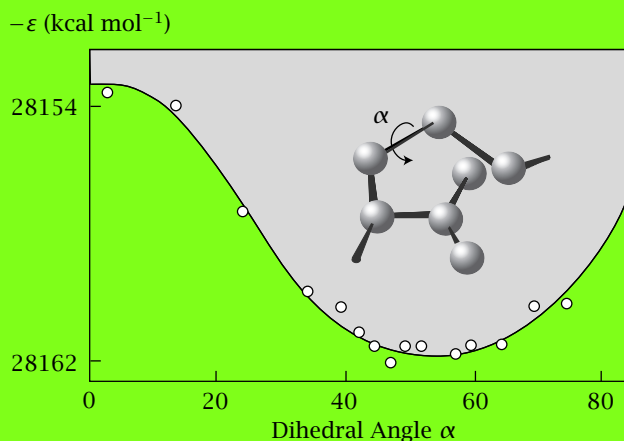
since q doesn't depend on V .

$$(e) \quad H = \Delta U + pV = \Delta U \implies \frac{H}{NkT} = \left(\frac{h\nu}{kT} \right) \left(\frac{e^{-h\nu\beta}}{1 - e^{-h\nu\beta}} \right)$$

8. Orbital steering in proteins.

To prove that proteins do not require 'orbital steering,' a process once proposed to orient a substrate with high precision before binding, T. Bruce has calculated the dependence of the total energy on the rotational conformation of the hydroxymethylene group of 4-hydroxybutyric acid at $T = 300$ K. Assume that the curve in the figure below is approximately parabolic, $\varepsilon = (1/2)k(\alpha - \alpha_0)^2$, where α is the dihedral angle of rotation. Use the equipartition theorem.

- Determine the spring constant k .
- What is the average energy $\langle \varepsilon \rangle$?
- What is the rms dihedral angle $\langle \alpha^2 \rangle^{1/2}$?



Source: TC Bruce, *Cold Spring Harbor Symposia on Quantitative Biology* **36**, 21–27 (1972).

Define the point $\alpha = 0$ to be at about 54° , the minimum in the curve. Take two points:

$$\varepsilon_0 = 0 \quad \alpha_0 = 0$$

$$\varepsilon_1 = 5.3 \quad \alpha_1 = 30^\circ \quad \text{to determine the parabola}$$

$$5.3 \frac{\text{kcal}}{\text{mol}} = \frac{1}{2} c (30^\circ)^2$$

$$(a) \quad \Rightarrow c = 1.2 \times 10^{-2} \frac{\text{kcal}}{\text{mole deg}^2}$$

$$(b) \quad \langle \varepsilon \rangle = \frac{kT}{2} \text{ by equipartition since}$$

$$\langle \varepsilon \rangle = \frac{\int_{-30}^{+30} \frac{c\alpha^2}{2} e^{-\frac{c\alpha^2}{2kT}} d\alpha}{\int_{-30}^{+30} e^{-\frac{c\alpha^2}{2kT}} d\alpha} = \frac{\frac{c}{2} \sqrt{\pi} \left(\frac{2kT}{c} \right)^{3/2}}{2 \sqrt{\frac{2\pi kT}{c}}} \quad \text{so} \quad \langle \varepsilon \rangle = 0.3 \frac{\text{kcal}}{\text{mol}}$$

(c) Note that α^2 is the same integral as above, except without the $c/2$ in the numerator, i.e.,

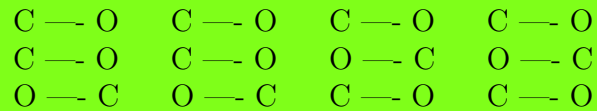
$$\langle \alpha^2 \rangle = \frac{\int \alpha^2 e^{-\frac{c\alpha^2}{2kT}}}{\int e^{-\frac{c\alpha^2}{2kT}} d\alpha} \quad \text{so}$$

$$\langle \alpha^2 \rangle = \frac{\langle \varepsilon \rangle}{\frac{c}{2}} = \frac{kT}{2 \left(\frac{c}{2} \right)} = \frac{kT}{c}$$

$$\begin{aligned} \langle \alpha^2 \rangle^{1/2} &= \left(\frac{kT}{c} \right)^{1/2} \\ &= \left(\frac{0.6 \text{kcal/mol}}{1.2 \times 10^{-2} \text{kcal/mol deg}^2} \right)^{1/2} \\ &= 7.07 \text{ degrees} \end{aligned}$$

9. The entropy of crystalline carbon monoxide at $T = 0\text{K}$.

Carbon monoxide doesn't obey the 'third law' of thermodynamics: that is, its entropy is not zero when the temperature is zero. This is because molecules can pack in either the C — O or O — C direction in the crystalline state. For example, one packing arrangement of twelve CO molecules could be:



Calculate the partition function and the entropy of a carbon monoxide crystal at $T = 0\text{K}$.

Since each CO molecule is distinguishable and has 2 possible orientations, then $q = 2$ and $\frac{S_{\text{CO,crystal}}}{R} = \ln Q = \ln 2^n = n \ln 2$, where n is the number of moles of CO.

10. Temperature dependent quantities in statistical thermodynamics.

Which quantities depend on temperature?

- (a) Planck's constant h
- (b) partition function q
- (c) energy levels ε_j
- (d) average energy $\langle \varepsilon \rangle$
- (e) heat capacity C_V for an ideal gas.

The temperature dependent quantities are (b) and (d).

11. Heat capacities of liquids.

- (a) C_V for liquid argon (at $T = 100\text{ K}$) is $18.7\text{ J(K mol)}^{-1}$. How much of this heat capacity can you rationalize on the basis of your knowledge of gases?
- (b) C_V for liquid water at $T = 10^\circ\text{ C}$ is about 75 J(K mol)^{-1} . Assuming water has three vibrations, how much of this heat capacity can you rationalize on the basis of gases? What is responsible for the rest?

- (a) Liquid argon is spherical (no rotations and no vibrations), and has only translational freedom, so

$$\begin{aligned}C_V &= \frac{3}{2}nR \\&= n\left(\frac{3}{2}\right)\left(8.314\frac{\text{J}}{\text{K mol}}\right) \\&= 12.47\frac{\text{J}}{\text{K mol}}\end{aligned}$$

can be rationalized. The rest must be due to intermolecular interactions.

- (b) $\frac{3}{2}nR$ due to translations, plus 0 or $3nR$ for vibrations depending whether they are strong or weak, plus $\frac{3}{2}nR$ for rotations equals $3nR = 24.94\frac{\text{J}}{\text{K mol}}$. The rest must be rationalized based on intermolecular interactions and hydrogen bonding.

12. The entropies of CO.

- (a) Calculate the translational entropy for carbon monoxide CO (C has mass $m = 12\text{ amu}$, O has mass $m = 16\text{ amu}$) at $T = 300\text{ K}$, $p = 1\text{ atm}$.
- (b) Calculate the rotational entropy for CO at $T = 300\text{ K}$. The CO bond has length $R = 1.128 \times 10^{-10}\text{ m}$.

Here the gas molecules are indistinguishable. This means that we need to include the correction $1/N!$ in the translation partition function of the N -particle system.

$$\begin{aligned}
\text{(a)} \quad S &= Nk \ln \left(\frac{qe}{N} \right) + \frac{\Delta U}{T} \\
&= nR \left(1 + \ln \left(\frac{q}{N} \right) \right) + \frac{3nR}{2} \\
S &= nR \left\{ \frac{5}{2} + \ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\frac{V}{N} \right) \right\} \\
\frac{S}{n} &= R \left\{ \frac{5}{2} + \ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \left(\frac{kT}{p} \right) \right\} \\
m &= (28)(1.78 \times 10^{-27} \text{ kg}) \\
kT &= (1.38 \times 10^{23} \text{ J/K})(300 \text{ K}) \\
p &= 1.013 \times 10^5 \text{ N/m}^2 \\
h^2 &= [6.626 \times 10^{-34} \text{ Js}]^2 \\
R &= 8.314 \text{ J/K mol} \\
\Rightarrow \frac{S}{n} &= 150.3 \frac{\text{J}}{\text{K mol}}
\end{aligned}$$

$$\begin{aligned}
\text{(b)} \quad \frac{S}{n} &= R[\ln q + 1] \\
q &= \frac{8\pi^2 \mu R^2 kT}{\sigma h^2} \\
\sigma &= 1 \\
\mu &= \frac{(12)(16)}{12 + 16} \\
&= (6.86) \times (1.67 \times 10^{-27} \text{ kg}) \\
\frac{S_{\text{rot}}}{n} &= 47.28 \text{ J/K mol.}
\end{aligned}$$

13. Conjugated polymers: why the absorption wavelength increases with chain length.

Polyenes are linear double-bonded polymer molecules $(\text{C}=\text{C})_N$, where N is the number of $\text{C}=\text{C}$ monomers. Model a polyene chain as a box in which π -electrons are particles that can move freely. If there are $2N$ carbon atoms each separated by bond length $d = 1.4 \text{ \AA}$, and if the ends of the box are a distance d past the end C atoms, then the length of the box is $\ell = (2N + 1)d$. An energy level, representing the two electrons in each bond, is occupied by two paired electrons. Suppose the N lowest levels are occupied by electrons, so the wavelength absorption of interest involves the excitation from level N to level $N + 1$. Compute the absorption energy $\Delta\varepsilon = \varepsilon_{N+1} - \varepsilon_N = hc/\lambda$ where c is the speed of light and λ is the wavelength of absorbed radiation, using the particle-in-a-box model.

The particle-in-a-box Equation (11.12) gives

$$\varepsilon_N = \frac{N^2 h^2}{8m\ell^2}$$

where m is the mass of an electron, so

$$\begin{aligned}\Delta\varepsilon = \varepsilon_{N+1} - \varepsilon_N &= \frac{h^2}{8md^2} \left[\frac{(N+1)^2 - N^2}{(2N+1)^2} \right] \\ &= \frac{h^2}{8md^2(2N+1)} \\ &= \frac{(6.626 \times 10^{-34} \text{ Js})^2 (6.02 \times 10^{23} \text{ molec/mole})}{8(9.11 \times 10^{-31} \text{ kg})(1.4 \times 10^{-10} \text{ m})^2 (2N+1)} \\ &= \frac{1.8 \times 10^3 \text{ kJ/mol}}{(2N+1)} = \frac{hc}{\lambda}\end{aligned}$$

so the wavelength λ increases in proportion to N . The quantitative accuracy of this model is not high, but the qualitative trend is correct.

14. Why are conjugated bonds so stiff?

As in problem 13, model polyene chain boxes of length $\ell \approx 2Nd$, where d is the average length of each carbon-carbon separation, and $2N$ is the number of carbons. There are $2N$ electrons in N energy levels, particles distributed throughout ‘boxes,’ according to the Pauli principle, with at most two electrons per level.

- (a) Compute the total energy.
- (b) Compute the total energy if the chain is ‘bent,’ that is if there are two boxes, each of length $\ell/2$ containing N electrons each.

(a) From equation (11.8), we have

$$\varepsilon_n = \frac{(nh)^2}{8m\ell^2} \quad n = 1, 2, 3, \dots$$

so the total energy E of $2N$ electrons is

$$\begin{aligned} E = \sum_{n=1}^N \varepsilon_n &= \frac{2h^2}{8m(nd)^2} \sum_{n=1}^N n^2 = \frac{h^2}{4m\ell^2} \frac{N(N+1)(2N+1)}{6} \\ &= \frac{h^2}{4md^2} \frac{(N+1)(2N+1)}{6N}. \end{aligned}$$

(b) For the bent chain,

$$E_b = \frac{4h^2}{8m\left(\frac{N^2d^2}{4}\right)} \sum_{n=1}^{N/2} n^2 = \frac{h^2}{2md^2} \frac{(N+1)(N+2)}{6N}.$$

The difference is

$$\begin{aligned} E_b - E &= \frac{h^2}{8md^2} \left[\frac{4(N+1)(N+2) - 2(N+1)(2N+1)}{6N} \right] \\ &= \frac{h^2}{8md^2} \frac{(N+1)}{N}. \end{aligned}$$

Since $h^2/(8md^2) \simeq 1.8 \times 10^3$ kJ/mol (see Problem 13), these bonds are predicted to be very stiff, according to this simple model.

15. Electrons flowing in wires carry electrical current.

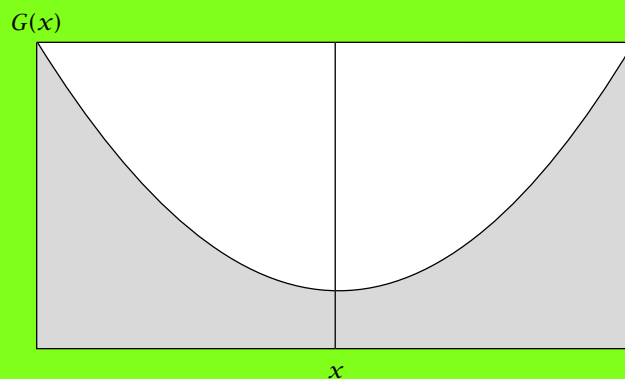
Consider a wire 1 m long and 10^{-4} m^2 in cross-sectional area. Consider the wire to be a box, and use the particle-in-a-box model to compute the translational partition function of an electron at $T = 300 \text{ K}$.

The particle-in-a-box partition function is (Eq 11.18):

$$\begin{aligned}
 q &= \left[\frac{2\pi m k T}{h^2} \right]^{3/2} V \\
 &= \left[\frac{2\pi (9.11 \times 10^{-31} \text{ kg}) (1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}) (300 \text{ K})}{(6.63 \times 10^{-34} \text{ J s})^2} \right]^{3/2} (10^{-4} \text{ m}^3) \\
 &= 1.25 \times 10^{21} \text{ states}
 \end{aligned}$$

16. Fluctuations.

A stable state of a thermodynamic system can be described by the free energy $G(x)$ as a function of the degree of freedom x . Suppose G obeys a square law, with spring constant k_s , $G(x)/kT = k_s x^2$ as shown in figure below.

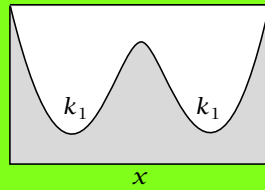


(a) Compute the mean square thermal fluctuations $\langle x^2 \rangle$ in terms of k_s .

- (b) Some systems have two single minima, with large spring constants k_1 , and others have a single broad minimum with small spring constant k_2 as shown in figures (a) and (b) below. For example, two-state equilibria may have two single minima, and the free energies near critical points have a single broad minimum. If $k_2 = 1/4k_1$, what is the ratio of fluctuations $\langle x_2^2 \rangle / \langle x_1^2 \rangle$ for individual energy wells?

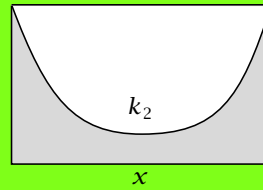
(a) Two Single Minima

$G(x)$



(b) One Broad Minimum

$G(x)$



$$\begin{aligned}
 \text{(a)} \quad \langle x^2 \rangle &= \frac{2 \int_0^\infty x^2 e^{-k_s x^2} dx}{2 \int_0^\infty e^{-k_s x^2} dx} \\
 &= \frac{\frac{1}{4k_s} \sqrt{\frac{\pi}{k_s}}}{\frac{1}{2} \sqrt{\frac{\pi}{k_s}}} \\
 &= \frac{1}{2k_s}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad \frac{\langle x_2^2 \rangle}{\langle x_1^2 \rangle} &= \frac{\frac{1}{k_2}}{\frac{1}{k_1}} \\
 &= \frac{\frac{1}{(\frac{1}{4})k_1}}{\frac{1}{k_1}} = 4
 \end{aligned}$$

17. Heat capacity for Cl₂

What is C_V at 800 K for Cl₂ treated as an ideal diatomic gas in the high-temperature limit?

For a diatomic molecule in the classical limit, there is a contribution to U of $(3/2)NkT$ from translation, NkT from rotation, and NkT from vibration in the high-temperature limit. Then total $U = (7/2)NkT$. Thus

$$\begin{aligned}C_V &= \left(\frac{\partial U}{\partial T} \right)_V \\&= \frac{7}{2} Nk.\end{aligned}$$

For one mole, C_V is

$$\begin{aligned}\frac{7}{2}R &= \frac{7}{2} \left(1.987 \frac{\text{cal}}{\text{K mol}} \right) \\&= 6.95 \frac{\text{cal}}{\text{K mol}}.\end{aligned}$$

18. Protein-in-a-box.

Consider a protein of diameter 40 \AA trapped in the pore of a chromatography column. The pore is a cubic box, 100 \AA on a side. The protein mass is 10^4 g mol^{-1} . Assume the box is otherwise empty and $T = 300 \text{ K}$.

- (a) Compute the translational partition function. Are quantum effects important?
- (b) If you deuterate all the hydrogens in the protein and increase the protein mass by 10%, does the free energy increase or decrease?
- (c) By how much?

- (a) Assuming that the protein is ideal and takes up no volume, so the available translational space is 100 Angstroms on each side:

$$\begin{aligned}
q_t &= \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \\
&= \left(\frac{2\pi(10^4 \frac{\text{g}}{\text{mol}})(10^{-3} \frac{\text{kg}}{\text{g}})(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}})(300\text{K})}{(6.02 \times 10^{23} \frac{1}{\text{mol}})(6.63 \times 10^{-34} \text{ J s})^2} \right)^{3/2} (10^{-10} \text{ m})^3 \\
&= 9.77 \times 10^{11} \quad \text{quantum effects are not important}
\end{aligned}$$

If we consider, though, that the protein is 40 Angstroms in diameter, that leaves only 60 Angstroms free for motion in each direction. This can be corrected for by multiplying by $(0.6)^3$, giving $q_t = 2.11 \times 10^{11}$, so quantum effects are still not important even with excluded volume taken into account.

(b) $F = -kT \ln Q$, so

$$\begin{aligned}
\Delta F &= -kT(\ln Q_2 - \ln Q_1) \\
&= -kT \ln \left(\frac{Q_2}{Q_1} \right) \\
&= -\frac{3NkT}{2} \ln(1.1) \\
&\Rightarrow \frac{F_2 - F_1}{NkT} = -0.143 \\
&\Rightarrow \text{free energy decreases (becomes more negative).}
\end{aligned}$$

$$(c) \quad \frac{\Delta F}{n} = -0.143RT = -86 \frac{\text{cal}}{\text{mol}}$$

19. Vibrational partition function of Iodine.

Compute the value of the vibrational partition function for iodine, I_2 , at $T = 308\text{K}$. (HINT: see table 11.2)

$$\begin{aligned}
q_{vib} &= \frac{e^{-\frac{h\nu}{2kT}}}{1 - e^{-\frac{h\nu}{kT}}} = \frac{e^{-\frac{\theta}{2T}}}{1 - e^{-\frac{\theta}{T}}}, \theta_{I_2} = 308 \\
\Rightarrow q_{vib} &= \frac{e^{-\frac{308}{2 \cdot 308}}}{1 - e^{-\frac{308}{308}}} = \frac{e^{-0.5}}{1 - e^{-1}} \approx \frac{0.6065}{1 - 0.3689} = \frac{0.6065}{0.6321} = 0.9595
\end{aligned}$$

20. Electron in a quantum-dot box.

An electron moving through the lattice of a semiconductor has reduced inertia. Assume that the effective mass of the electron is only 10% of its actual mass at rest. Calculate the translational partition function of the electron at room temperature (273° K) in a small semiconductor particle of a cubic shape with a side

- (a) 1 mm (10^{-3}m),
- (b) 100 Å ($100 \cdot 10^{-10}\text{m}$);
- (c) To which particle would the term quantum dot, i.e. system with quantum mechanical behavior, be applied, and why?

- (a) $q_{\text{transl}} = \left(\frac{2\pi m'_e kT}{h^2}\right)^{3/2} V$
 $m'_e = 0.1m_e = 0.1 \cdot 9.11 \cdot 10^{-31}\text{kg}$
 $k = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$
 $h = 6.63 \cdot 10^{-34} \text{Js}$
 $q_{\text{transl}} = \left(\frac{2 \cdot 3.14 \cdot 0.1 \cdot 9.11 \cdot 10^{-31} \cdot 1.38 \cdot 10^{-23} \cdot 273}{(6.63 \cdot 10^{-34})^2}\right)^{3/2} V = 3.43 \cdot 10^{23} \cdot V \text{ states}$
 $q_{\text{transl}} = 3.43 \cdot 10^{23} \cdot (10^{-3})^3 = 3.43 \cdot 10^{14} \text{ states}$
- (b) $q_{\text{transl}} = 3.43 \cdot 10^{23} \cdot (10^{-8})^3 = 0.343 \text{ states.}$
- (c) The latter system has just a few states and will behave in a quantum mechanical way. Thus, the term quantum dot can be applied to the smaller system.

21. A protein, quantum mechanics and the cell.

Let us assume for a moment that a protein of mass 50,000 g/mol can freely move in the cell. Approximate the cell as a cubic box 10 μm on a side.

- (a) Compute the translational partition function for the protein in the whole cell. Are quantum effects important?
- (b) The living cell, however, is very crowded with other molecules. Now assume that the protein can freely move only 5 Å along each, x -, y - and z -direction before it bumps into some other molecule. Compute the translation partition function and conclude whether quantum mechanical effects are important in this case.
- (c) Now assume that we deuterate all the hydrogens in the protein (replace hydrogens with deuterium atoms). If the protein mass is increased by 10%, what happens to the free energy of the modified protein? By how much does it change?

$$(a) \quad q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V = \left(\frac{2 \cdot 3.1415 \cdot (50 \text{ kg/mol}) (1.38 \cdot 10^{-23} \text{ J/K}) (300 \text{ K})}{(6.02 \cdot 10^{23})^2}\right)^{3/2} (10^{-15} \text{ m}^3) \\ = (4.9 \cdot 10^{-23-23})^{3/2} \cdot 10^{-15} \approx 10^{34} \cdot 10^{-15} = 10^{19} \\ \text{Quantum effects are not important.}$$

$$(b) \quad q_t = 10^{34} \cdot (5 \cdot 10^{-10} \text{ m})^3 \approx 10^{34} \cdot 125 \cdot 10^{-30} = 1.25 \cdot 10^6 \\ \text{Quantum effects can still be ignored.}$$

$$(c) \quad F = -kT \ln Q \\ \Delta F = -kT (\ln Q_2 - \ln Q_1) = -kT \ln\left(\frac{Q_2}{Q_1}\right) = -NkT \left(\frac{m_2}{m_1}\right)^{3/2} = \frac{F_2 - F_1}{NkT} = -0.143 \\ \text{Decreases.} \\ \text{Change per one molecule:} \\ \frac{F_2 - F_1}{NkT} = -0.143 \cdot (1.38 \cdot 10^{-23} \text{ J/K}) \cdot 300 \text{ K} = 5.92 \cdot 10^{-22} \text{ J}$$

22. Electron in benzene.

Consider an electron that can move freely throughout the aromatic orbitals of benzene. Model the electron as a particle in a 2-dimensional box $4 \text{ Å} \times 4 \text{ Å}$.

- (a) Compute $\Delta\epsilon$, the energy change from the ground state to the first excited state, $n_x = n_y = 2$.
- (b) Compute the wavelength λ of light that would be absorbed in this transition, if $\Delta\epsilon = \frac{hc}{\lambda}$, where h = Planck's constant and c = speed of light.
- (c) Will this transition be in the visible part of the electromagnetic spectrum (i.e., is liquid benzene colored or transparent), according to this simple model?

- (a) $\epsilon(n_x, n_y) = \frac{h^2}{8ml^2}(n_x^2 + n_y^2)$.
 $\Delta\epsilon = \epsilon(2, 2) - \epsilon(1, 1) = \frac{3h^2}{4ml^2} = \frac{3(6.626 \cdot 10^{-34} Js)^2}{4(9 \cdot 10^{-31} kg)(4 \cdot 10^{-10} m)^2}$
 $\Delta\epsilon = (2.27 \cdot 10^{-18} \frac{J}{electron})(6 \cdot 10^{23} \frac{electrons}{mol}) = 1.37 \cdot 10^6 \frac{J}{mol}$
- (b) $\lambda = \frac{hc}{\Delta\epsilon} = \frac{(6.626 \cdot 10^{-34} Js)(3 \cdot 10^8 m/s)}{2.27 \cdot 10^{-18} J} = 8.8 \cdot 10^{-8} m$.
- (c) Using Figure 10.2, this is in the UV-visible range.

23. Vibrational in insulin.

What is the average energy stored in the vibration degrees of freedom of one molecule of insulin, a protein with $C_{256}H_{381}N_{65}O_{76}S_6$, at room temperature?

There are $N = 256 + 381 + 65 + 76 + 6 = 784$ atoms in the molecule.
 $\langle\epsilon\rangle_{vib} = (3N - 6) \cdot \frac{1}{2}kT = (3 \cdot 784 - 6) \cdot 150 \cdot 1.38 \cdot 10^{-23} = 4.85 \cdot 10^{-18} J$
 $\langle\theta\rangle_{vib} = \frac{4.85 \cdot 10^{-18}}{1.38 \cdot 10^{-23}} = 351,449 K$

24. Escape velocity of gases from the moon.

The escape velocity of an object to leave the moon is 3.4 km/s. The temperature on the sunny surface of the moon is 400 K. What is the weight of the gas which will escape the moon with an average velocity $\langle V_x^2 \rangle^{1/2}$. Draw a short conclusion from the result.

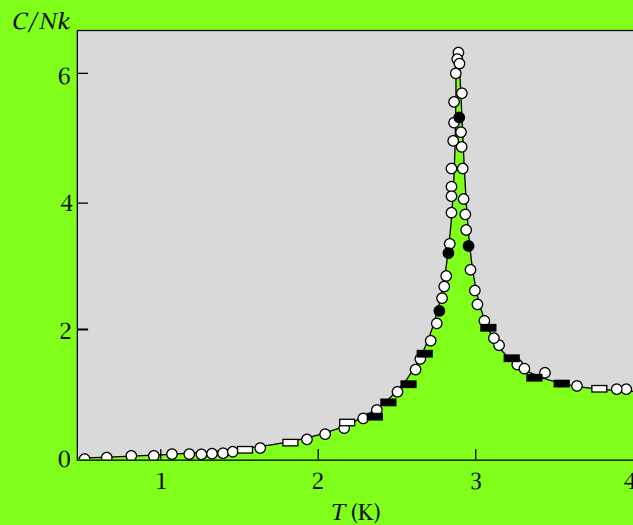
$\frac{1}{2}m\langle V_x^2 \rangle^{1/2} = \frac{1}{2}kT$
 $m = \frac{kT}{\langle V_x^2 \rangle^{1/2}} = \frac{400 \cdot 1.38 \cdot 10^{-23}}{3400^2} = 4.78 \cdot 10^{-28} kg = 4.78 \cdot 10^{-25} g$
 $m \text{ (in g/mol)} = 4.78 \cdot 10^{-25} \cdot 6.022 \cdot 10^{23} = 0.29 g/mol$
 No gas will escape the Moon.

Chapter 12

Temperature, Heat Capacity

1. Heat capacity peaks from phase transitions.

The peak heat capacity in the figure below shows that helium gas adsorbed on graphite undergoes a transition from an ordered state at low temperature to a disordered state at high temperature. Use the figure below to estimate the energy associated with the transition.



Source: HJ Kreuzer and ZW Gortel, *Physisorption Kinetics*, Springer Verlag, Heidelberg, 1986. Data are from RL Elgin and DL Goodstein, *Phys Rev A* **9**, 2657–2675 (1974); *Proceedings of the 13th International Conference on Low Temperature Physics*, edited by KD Timmerhaus, WJ O’Sullivan and EF Hammel, Plenum, New York.

The peak in the heat capacity suggests that some kind of bond or interaction breaks at a temperature of about $T = 3\text{K}$. A characteristic energy can be computed from

$$\varepsilon = kT = \left(1.987 \frac{\text{cal}}{\text{mol deg}}\right) (3\text{K}) \cong 6 \frac{\text{cal}}{\text{mol}}.$$

Since this heat capacity peak is much narrower than in the two-state model, it shows that the two-state model would not be an adequate way to model this. We also need to account for cooperativity.

2. Two-state model of a hydrogen bond.

Suppose a hydrogen bond in water has an energy of about 2 kcal mol^{-1} . Suppose a ‘made’ bond is the ground state in a two-state model and a ‘broken’ bond is the excited state. At $T = 300 \text{ K}$, what fraction of hydrogen bonds are broken?

Use Equation (12.4),

$$\begin{aligned} \ln \left(\frac{f_{\text{gnd}}}{f_{\text{exc}}} \right) &= \frac{\varepsilon}{kT} \\ &= \frac{2000 \text{ cal/mol}}{(2 \text{ cal/mol})(300 \text{ K})} \\ &= 3.33 \end{aligned}$$

$$\Rightarrow \left(\frac{f_{\text{gnd}}}{f_{\text{exc}}} \right) \cong 29 \quad \text{so}$$

$$\frac{f_{\text{exc}}}{f_{\text{exc}} + f_{\text{gnd}}} = \frac{1}{1 + f_{\text{gnd}}/f_{\text{exc}}} = \frac{1}{29} \cong 3.4\%$$

of the bonds are broken.

3. A random energy model of glasses.

Glasses are materials that are disordered—and not crystalline—at low temperatures. Here's a simple model. Consider a system that has a Gaussian distribution of energies E , according to Equation (12.16):

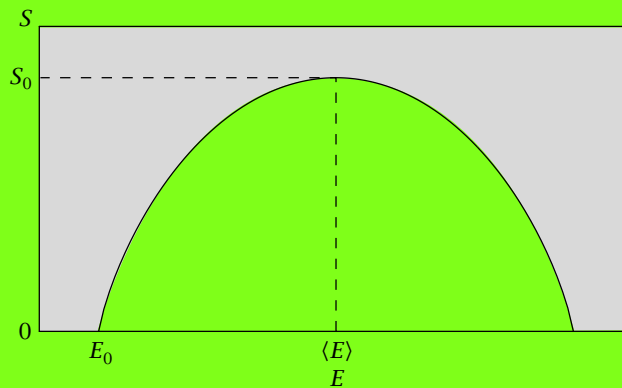
$$p(E) = p_0 \exp \left[-(E - \langle E \rangle)^2 / 2\Delta E^2 \right],$$

where $\langle E \rangle$ is the average energy and ΔE characterizes the magnitude of the fluctuations, that is, the width of the distribution.

- (a) Derive an expression showing that the entropy $S(E)$ is an inverted parabola,

$$S(E) = S_0 - \frac{k(E - \langle E \rangle)^2}{2\Delta E^2}.$$

- (b) An *entropy catastrophe* happens (left side of the curve in the figure below where $S = 0$). For any physical system, the minimum number of accessible states is $W = 1$, so $S = k \ln W$ implies that the minimum entropy is $S = 0$. At the point of the entropy catastrophe, the system has no states that are accessible below an energy $E = E_0$. Compute E_0 .
- (c) The *glass transition temperature* T_g is the temperature of the entropy catastrophe. Compute T_g from this model.



- (a) Substitute $p(E)$ into $S(E) = k \ln p(E)$ to get:

$$\frac{S}{k} = \ln p_0 - \frac{(E - \langle E \rangle)^2}{2\Delta E^2}.$$

Defining $S_0 = k \ln p_0$, this becomes

$$S(E) = S_0 - \frac{k (E - \langle E \rangle)^2}{2\Delta E^2}.$$

(b) At $S = 0$, the entropy equation gives

$$\begin{aligned} 0 &= S_0 - \frac{k (E_0 - \langle E \rangle)^2}{2\Delta E^2} \\ 12(a) \quad &\implies (E_0 - \langle E \rangle)^2 = \frac{2\Delta E^2 S_0}{k} \\ &\implies E_0 = \langle E \rangle - \Delta E \sqrt{\frac{2S_0}{k}}. \end{aligned}$$

(c) Substitute the entropy equation $S(E)$ into the definition of temperature, evaluated at the point $E = E_0$:

$$\begin{aligned} \frac{1}{T_g} &= \left. \frac{\partial S}{\partial E} \right|_{E_0} \\ &= \left. \frac{-k (E - \langle E \rangle)}{\Delta E^2} \right|_{E_0}. \end{aligned}$$

Now substituting the square root of Equation 12(a) into this expression gives

$$12(b) \quad \frac{1}{T_g} = \frac{k}{\Delta E^2} \sqrt{\frac{2\Delta E^2 S_0}{k}}.$$

(The minus sign has disappeared because Equation 12(a) has two roots, one positive and one negative. Since our interest is in the left side of the $S(E)$ curve, $T_g > 0$.) Rearranging Equation 12(b) gives

$$T_g = \sqrt{\frac{\Delta E^2}{2kS_0}}.$$

For more details, see Onuchic et al (1997).

4. Fluctuations in enthalpy.

The mean square fluctuations in enthalpy for processes at constant pressure are given by an expression similar to Equation (12.17) for processes at constant pressure:

$$\langle \delta H^2 \rangle = \langle (H - \langle H \rangle)^2 \rangle = kT^2 C_p.$$

What is the root-mean-square enthalpy fluctuation $\langle \delta H^2 \rangle^{1/2}$ for water at $T = 300$ K?

$$\begin{aligned} \langle \delta H^2 \rangle^{1/2} &= (kT^2 C_p)^{1/2} \\ &= \left[\left(2 \frac{\text{cal}}{\text{mol K}} \right) (300 \text{ K})^2 \left(18 \frac{\text{cal}}{\text{mol K}} \right) \right]^{1/2} \\ &= 1.8 \frac{\text{kcal}}{\text{mol}} \end{aligned}$$

5. Oxygen vibrations.

Oxygen molecules have a vibrational frequency of 1580 cm^{-1} (see Example 11.3). If the relative populations are $f_{\text{ground}}/f_{\text{excited}} = 100$ in the Schottky model, what is the temperature of the system?

$$\begin{aligned} \frac{1}{T} &= \left(\frac{k}{\varepsilon_0} \right) \ln \left(\frac{f_{\text{gnd}}}{f_{\text{exc}}} \right) \\ &= \left(\frac{k}{h\nu} \right) \ln \left(\frac{f_{\text{gnd}}}{f_{\text{exc}}} \right) \\ &= \left(\frac{1}{\theta_{\text{vib}}} \right) \ln \left(\frac{f_{\text{gnd}}}{f_{\text{exc}}} \right) \\ &= \frac{1}{2274} \ln(1000) \\ \implies T &= \frac{2274}{\ln(1000)} = 329 \text{ K} \end{aligned}$$

6. Modeling a population inversion.

Population inversion, when more particles of a system are in an excited state than a ground state, is used to produce laser action. Consider a system of atoms at 300 K with 3 energy levels: 0 kcal/mol, 0.5 kcal/mol, and 1.0 kcal/mol. For this problem, please use 5 decimal places.

- Compute the probabilities p_1^* , p_2^* , and p_3^* that an atom is in each energy level.
- What is the average energy $\langle \epsilon \rangle$ of the system? What is the entropy (in cal/mol·K) of the system?
Now suppose you excite the system to cause a population inversion, resulting in a new population distribution p^{**} as follows: $p_1^{**} = p_3^*$, $p_2^{**} = p_2^*$, $p_3^{**} = p_1^*$.
- What is the average energy $\langle \epsilon \rangle$ of the system after the population inversion? What is the entropy (in cal/mol·K) of the system after the population inversion?
- What is the temperature of the system after the population inversion?

- $Q = \sum_{j=1}^t e^{-\frac{\epsilon_j}{kT}} = 1 + 0.434233 + 0.18691 = 1.61924$
 $p_1^* = \frac{1}{1.61924} = 0.61757$, $p_2^* = \frac{0.434233}{1.61924} = 0.26700$, $p_3^* = \frac{0.18691}{1.61924} = 0.11543$
- $\langle \epsilon \rangle = \sum_{j=1}^t p_j \cdot E_j = 248.93 \frac{\text{cal}}{\text{mol}}$
 $S = -k \sum_{j=1}^t p_j \ln(p_j) = 1.78 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$
- Using new p^{**} , $\langle \epsilon \rangle = 751.07 \frac{\text{cal}}{\text{mol}}$
 $S = 1.78 \frac{\text{cal}}{\text{mol} \cdot \text{K}}$ (Same as in part 2 since the entropy should not change.)
- $p_3^{**} = p_1^* = \frac{e^{-\frac{\epsilon_j}{kT}}}{q} = \frac{e^{-\frac{503.14779}{T}}}{1 + e^{-\frac{251.57390}{T}} + e^{-\frac{503.14779}{T}}} = 0.61757$
 $\Rightarrow T = -300K$
 Would also accept:
 $\frac{1}{t} = \frac{k}{\epsilon} \ln\left(\frac{f_{\text{gnd}}}{f_{\text{exc}}}\right)$ since $p_2^{**} = p_2^*$

7. Schottky model for hydrogen.

Hydrogen molecules have a vibrational frequency of 4300 cm^{-1} . If 0.5% of the molecules are in the excited state, what is the temperature of the system?

$$\frac{1}{T} = \frac{1}{\theta_{vib}} \ln \left[\frac{99.5}{0.5} \right] \text{ where } \theta_{vib} = \frac{h\nu}{k}$$

$$\theta_{vib} = \frac{(6.626 \cdot 10^{-34})(4300)(2.994 \cdot 10^{10})}{1.38 \cdot 10^{-23}} = 6187.67$$

So: $T = 1168K$

8. Finding the C_v of a gas.

A gas is placed in an airtight container. A piston decreases the volume by 10% in an adiabatic process, and the temperature is observed to increase by 10%. What is the constant-volume heat capacity of the gas?

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\frac{Nk}{C_v}}$$

$$\frac{110}{100} = \left(\frac{100}{90} \right)^{\frac{Nk}{C_v}}$$

Take the Log of both sides:

$$\text{Log}(1.10) = \text{Log}(1.11) \cdot \frac{R}{C_v}$$

$$C_v = \frac{0.0453}{0.041} \left(2 \frac{\text{cal}}{\text{mol} \cdot K} \right) = 2.21 \frac{\text{cal}}{\text{mol} \cdot K}$$

Chapter 13

Chemical Equilibria

1. Iodine dissociation.

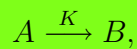
Compute the dissociation constant K_p for iodine, $I_2 \rightarrow 2I$, at $T = 300$ K.

Follow Example 13.3. But now

$$\begin{aligned}
 kT &= \left(\frac{300}{1000}\right) 1.363 \times 10^{-25} \text{ m}^3 \text{ atm} = 4.09 \times 10^{-26} \text{ m}^3 \text{ atm} \\
 e^{-\frac{\Delta \epsilon_0}{kT}} &= e^{-\frac{35,600}{(1.987)(300)}} = 1.16 \times 10^{-26} \\
 q_{rI_2} &= \left(\frac{300}{1000}\right) 9310 = 2793 \\
 q_{vI_2} &= \frac{1}{1 - e^{-\frac{308}{300}}} = 1.56 \\
 \frac{q_{tI}^2}{q_{tI_2}} &= \left(\frac{300}{1000}\right)^{3/2} 3.01 \times 10^{33} \text{ m}^{-3} = 4.95 \times 10^{32} \text{ m}^{-3} \\
 \text{so } K_p &= (4.09 \times 10^{-26} \text{ m}^3 \text{ atm})(1.15 \times 10^{-26}) \left(\frac{1}{2793}\right) \left(\frac{1}{1.56}\right) (16)(4.95 \times 10^{32} \text{ m}^{-3}) \\
 &= 8.5 \times 10^{-22} \text{ atm}
 \end{aligned}$$

2. Temperature dependence of a simple equilibrium.

In a reaction



the equilibrium constant is $K = 10$ at $T = 300\text{ K}$.

- (a) What is $\Delta\mu^\circ$?
- (b) If $\Delta h^\circ = 10\text{ kcal mol}^{-1}$, what is K at $T = 310\text{ K}$?
- (c) What is Δs° at $T = 300\text{ K}$?

$$\begin{aligned}\text{(a)} \quad \Delta\mu^\circ &= -RT\ln K \\ &= -(1.987 \frac{\text{cal}}{\text{K mol}})(300\text{K}) \ln(10) \\ &= -1.37 \frac{\text{kcal}}{\text{mol}}\end{aligned}$$

(b) The van't Hoff equation gives

$$\begin{aligned}\ln K_2 &= \ln K_1 - \frac{\Delta h^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\ &= \ln(10) - \frac{10,000 \frac{\text{cal}}{\text{mol}}}{2 \frac{\text{cal}}{\text{K mol}}} \left(\frac{1}{310} - \frac{1}{300} \right) \\ &= 2.303 + 0.5376 = 2.84 \\ \Rightarrow K_2 &= 17\end{aligned}$$

$$\begin{aligned}\text{(c)} \quad \Delta s^\circ &= \frac{\Delta h^\circ - \Delta\mu^\circ}{T} \\ &= \frac{(10,000 + 1,370) \frac{\text{cal}}{\text{mol}}}{300\text{K}} \\ &= 37.9 \frac{\text{cal}}{\text{K mol}}\end{aligned}$$

3. Dissociation of oxygen, $O_2 \rightleftharpoons 2O$.

Compute K_p , the pressure-based equilibrium constant for this dissociation reaction at $T = 3000$ K. The electronic ground-state degeneracy for O is $g_0(O) = 9$.

Similar to Example 13.3

$$K_p = kT \frac{\left[\left(\frac{2\pi m_{O_2} kT}{h^2} \right)^{3/2} \right]^2}{\left(\frac{2\pi m_{O_2} kT}{h^2} \right)^{3/2}} \frac{2\Theta_r(O_2)}{T} \left(1 - e^{-(\Theta_v(O_2)/T)} \right) \frac{g^2(O)}{g(O_2)} e^{-[D_0/(kT)]}$$

Since $m_{O_2} = 2m_O$, this simplifies to

$$K_p = \left(\frac{\pi m_O kT}{h^2} \right)^{3/2} \left(\frac{2\Theta_r R}{N_A} \right) \left(1 - e^{-(\Theta_v/T)} \right) \frac{g^2(O)}{g(O_2)} e^{-(D_0/kT)}$$

From Table 11.2

$$\begin{aligned} m_O &= \frac{0.016 \text{ kg}}{6.02 \times 10^{23}} = 2.66 \times 10^{-26} \text{ kg} \\ \Theta_r &= 2.08 \text{ K} \\ \Theta_v &= 2274 \text{ K} \\ D_0 &= 492 \frac{\text{kJ}}{\text{mol}} \\ g_0(O_2) &= 3 \\ g_0(O) &= 9 \quad \implies \quad g^2(O) = 81 \end{aligned}$$

So we compute that

$$\begin{aligned} \left(\frac{\pi m_O kT}{h^2} \right)^{3/2} &= \left[\frac{\pi (2.66 \times 10^{-26} \text{ kg}) (1.38 \text{ J/K}) (3000 \text{ K})}{[6.626 \times 10^{-34} \text{ Js}]^2} \right]^{3/2} \\ &= (7.88 \times 10^{21} \text{ m}^{-2})^{3/2} \approx 7.00 \times 10^{32} \text{ m}^{-3} \\ \left(\frac{2\Theta_r R}{N_A} \right) &= \frac{2(2.08 \text{ K}) (8.21 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1})}{6.02 \times 10^{23} \text{ molecules mol}^{-1}} \end{aligned}$$

$$= 5.67 \times 10^{-28} \text{ m}^3 \text{ atm}$$

$$(1 - e^{-\Theta_v/T}) = (1 - e^{-2274 \text{ K}/3000 \text{ K}}) = 0.531$$

$$\frac{g^2(O)}{g(O_2)} = \frac{81}{3} = 27$$

$$e^{-D_0/kT} = \exp\left(\frac{-492 \text{ kJ/mol}}{(8.314 \text{ J})(3000 \text{ K})}\right) = e^{-19.726} = 2.71 \times 10^{-9}$$

Substituting these values gives

$$K_p = (7.00 \times 10^{32} \text{ m}^{-3})(5.67 \times 10^{-28} \text{ m}^3 \text{ atm})(0.531)(27)(2.71 \times 10^{-9}) = 0.0154 \text{ atm}$$

4. Temperature dependence of K_p .

For the dissociation of O_2 , derive an expression for $d \ln K_p / dT$ near $T = 300 \text{ K}$ from the expression for K_p that you used in problem 3.

Start with

$$K_p = \left(\frac{\pi m_O kT}{h^2}\right)^{3/2} \left(\frac{2\Theta_r R}{N_A}\right) (1 - e^{-\frac{\Theta_v}{T}}) \frac{g^2(O)}{g(O_2)} e^{-\frac{D_0}{kT}}$$

Since $\frac{\Theta_v}{T} \gg 1$, $(1 - e^{-\frac{\Theta_v}{T}}) \approx 1$, so the temperature dependence can be expressed as

$$K_p(T) = C_0 T^{3/2} e^{-\frac{D_0}{kT}}.$$

$$\text{Therefore } \ln K_p = \ln C_0 + \frac{3}{2} \ln T - \frac{D_0}{kT}$$

$$\text{and } \frac{d \ln K}{dT} = \frac{3}{2T} + \frac{D_0}{kT^2}$$

Near $T = 300 \text{ K}$,

$$\begin{aligned}\frac{d \ln K}{dT} &= \frac{3}{2(300\text{K})} + \frac{492,000 \frac{\text{J}}{\text{mol}}}{(8.314 \frac{\text{J}}{\text{mol K}})(300\text{K})^2} \\ &= 5 \times 10^{-3} \text{ K}^{-1} + 0.65 \text{ K}^{-1} \approx 0.66 \text{ K}^{-1}\end{aligned}$$

It is clear that the term $\frac{D_0}{kT}$ dominates the temperature dependence.

5. Polymerization.

Consider a polymerization reaction in the gas phase in which n moles of identical monomers are in equilibrium with one mole of chains of n -mers:



- Do you expect typical polymerization processes to be driven, or opposed, by enthalpy? By entropy? What are the physical origins of these enthalpies and entropies?
- Do you expect polymerizations to be exothermic (giving off heat) or endothermic (taking up heat)? Explain the explosions in some polymerization processes.
- Are polymerization equilibrium constants for long chains more or less sensitive to temperature than for shorter chains?

- (a) The polymerization equilibrium $nA \xrightarrow{K} A_n$ is described by Eq 13.19

$$K = \frac{q_n}{q_1^n} e^{-\frac{(n-1)\Delta\epsilon_0}{kT}}$$

where q_1 is the partition function for the monomer, q_n is for a polymer chain, $\Delta\epsilon_0$ is the energy of forming one monomer-monomer bond in the chain, and n is the number of monomers in a chain.

(We're simplifying here - most polymers have distributions of molecular weight, rather than a single value n .)

Bond formation typically leads to $\Delta\epsilon_0 = \epsilon_{\text{bonded}} - \epsilon_{\text{notbonded}} < 0$, so it is driven by enthalpy and opposed by the translational entropy involved in bringing the monomers together in space and orienting them appropriately to react to form a bond. (See Ex. 13.3 for iodine dissociation.)

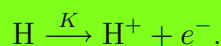
- (b) Since $\Delta\varepsilon_0 < 0$, the energy of the system is reduced by bond formation, so according to the first law, that energy must have left the system either as heat or work. These reactions are typically exothermic. The amount of heat given off is often large because of the factor $(n - 1)$ in the exponent of the above equation, where n can be greater than 10^3 ; this resulted in explosions in the early days of polymer chemistry.
- (c) The van't Hoff relation gives (approximately)

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta h^\circ}{kT^2} = \frac{(n - 1)\Delta\varepsilon_0}{kT^2}$$

so the slope of $\ln K$ versus T gets steeper as n gets larger. Hence, formation of longer chains is more sensitive to temperature than for shorter chains.

6. Hydrogen dissociation.

A hydrogen atom can dissociate in the gas phase:



Calculate the equilibrium constant K for temperature $T = 5000$ K. There is no rotational or vibrational partition function for H, H^+ , or e^- , but there are spin partition functions: $q_s = 1$ for H^+ , and $q_s = 2$ for e^- . $\Delta D = -311 \text{ kcal mol}^{-1}$.

$$\begin{aligned} K_p &= \frac{q_{\text{H}^+} q_{e^-}}{q_{\text{H}}} e^{-\frac{\Delta\varepsilon_0}{kT}} \\ &= kT \frac{\left[\frac{2\pi m_{\text{H}^+} kT}{h^2} \right]^{3/2} \left[\frac{2\pi m_e kT}{h^2} \right]^{3/2} e^{-\frac{\Delta\varepsilon_0}{kT}}}{\left[\frac{2\pi m_{\text{H}} kT}{h^2} \right]^{3/2}} \\ &= kT \left[\frac{2\pi m_e kT}{h^2} \right]^{3/2} e^{-\frac{\Delta\varepsilon_0}{kT}} \\ &= \frac{(8.21 \times 10^{-5} \frac{\text{m}^3 \text{atm}}{\text{K mol}})(5000 \text{K})}{6.02 \times 10^{23} \frac{\text{molecules}}{\text{mol}}} \\ &\quad \left\{ \frac{(2\pi)(9.11 \times 10^{-31} \text{kg})(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}})(5000 \text{K})}{(6.626 \times 10^{-34} \text{Js})^2} \right\}^{3/2} e^{-311,000/9935} \\ &= (6.82 \times 10^{-25} \text{ m}^3 \text{atm})(8.53 \times 10^{26} \text{ m}^{-3})(2.54 \times 10^{-14}) \\ &= 1.48 \times 10^{-11} \text{ atm} \end{aligned}$$

7. Free energy along the reaction coordinate.

Consider the ideal gas-phase equilibrium $2A \rightleftharpoons B$, at constant temperature and a constant pressure of 1 atm. Assume that there is initially 1 mole of A and no B present, and that $\mu_A^\circ = 5 \text{ kcal mol}^{-1}$ and $\mu_B^\circ = 10 \text{ kcal mol}^{-1}$ at this temperature.

(a) Show that G , at any time during the reaction, can be written as

$$G = \left(5 + RT \ln \left[\left(\frac{1-2\xi}{1-\xi} \right)^{1-2\xi} \left(\frac{\xi}{1-\xi} \right)^\xi \right] \right) \frac{\text{kcal}}{\text{mol}},$$

where ξ is the extent of reaction.

(b) What is the value of the extent of reaction ξ at equilibrium?

(a)
$$G = \sum_{i=1}^2 n_i \mu_i = n_A \mu_A + n_B \mu_B.$$

Let ξ represent the progress toward B :

$$d\xi = dn_B = -\frac{dn_A}{2}.$$

Integrating gives

$$\begin{aligned} n_B &= n_B(0) + \xi \\ n_A &= n_A(0) - 2\xi \end{aligned}$$

where $n_B(0)$ means the value of n_B when $\xi = 0$. Since there is initially 1 mole of A , $n_A(0) = 1$, $n_B(0) = 0$, so

$$\begin{aligned} n_B &= \xi \\ n_A &= 1 - 2\xi \\ n_{\text{total}} &= n_A + n_B = 1 - \xi. \end{aligned}$$

Now let's convert these quantities into pressures. The total pressure of the gas is the sum of the partial pressures

$$p = (n_A + n_B) \left(\frac{RT}{V} \right) = 1 \text{ atm.}$$

Therefore you can express the partial pressures as

$$\frac{p_A}{p} = \frac{n_A}{n_A + n_B} = \frac{1 - 2\xi}{1 - \xi}$$

and $\frac{p_B}{p} = \frac{n_B}{n_A + n_B} = \frac{\xi}{1 - \xi}$

The chemical potentials are

$$\mu_A = \mu_A^\circ + RT \ln \left(\frac{p_A}{p} \right), \quad \mu_B = \mu_B^\circ + RT \ln \left(\frac{p_B}{p} \right)$$

where $\mu_{A|B}^\circ$ is the chemical potential when $p_{A|B} = p = 1$ atm. Therefore Eq 13.a gives

$$\begin{aligned} G &= n_A \mu_A^\circ + n_A RT \ln \left(\frac{p_A}{p} \right) + n_B \mu_B^\circ + n_B RT \ln \left(\frac{p_B}{p} \right) \\ &= \left(5 \frac{\text{kcal}}{\text{mol}} \right) (n_A + 2n_B) + RT \ln \left[\left(\frac{p_A}{p} \right)^{n_A} \left(\frac{p_B}{p} \right)^{n_B} \right] \\ &= 5 \frac{\text{kcal}}{\text{mol}} + RT \ln \left[\left(\frac{1 - 2\xi}{1 - \xi} \right)^{1 - 2\xi} \left(\frac{\xi}{1 - \xi} \right)^\xi \right] \end{aligned}$$

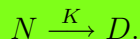
(b) At equilibrium, $\partial G / \partial \xi = 0$. Taking the derivative of G / RT gives

$$\begin{aligned} 2 \ln \left(\frac{1 - \xi}{1 - 2\xi} \right) + \ln \left(\frac{\xi}{1 - \xi} \right) - 2 + \left(\frac{1 - 2\xi}{1 - \xi} \right) + 1 + \left(\frac{\xi}{1 - \xi} \right) &= 0 \\ \implies \frac{\xi(1 - \xi)}{(1 - 2\xi)^2} &= 1 \\ \implies 1 - 5\xi + 5\xi^2 &= 0 \\ \implies \xi &= 0.276 \end{aligned}$$

The other solution, $\xi = 0.724$, gives a maximum in G , not a minimum, as you can see by checking the second derivative.

8. Pressure denaturation of proteins.

For a typical protein, folding can be regarded as involving two states, native (N) and denatured (D),



At $T = 300\text{ K}$, $\Delta\mu^\circ = 10\text{ kcal mol}^{-1}$. Applying about 10,000 atm of pressure can denature a protein at $T = 300\text{ K}$. What is the volume change Δv for the unfolding process?

We assume here that with the added 10,000 atm pressure, $K_2 = 1 \implies \Delta\mu_2^\circ = 0$. Therefore, following Example 13.6

$$\begin{aligned}\Delta v &= v_D - v_N = -\frac{RT(\ln K_2 - \ln K_1)}{\Delta p} = -\frac{RT(-\frac{\Delta\mu_2^\circ}{RT} - -\frac{\Delta\mu_1^\circ}{RT})}{\Delta p} \\ &= -\frac{(0 + 10,000)\frac{\text{cal}}{\text{mol}}}{10,000\text{ atm}} \left(\frac{8.21 \times 10^{-5}\frac{\text{m}^3\text{ atm}}{\text{K mol}}}{2\frac{\text{cal}}{\text{K mol}}} \right) \left(\frac{10^{10}\text{ \AA}}{\text{m}} \right)^3 \left(\frac{1\text{ mole}}{6.02 \times 10^{23}\text{ molecules}} \right) \\ &= 68 \frac{\text{\AA}^3}{\text{molecule}}\end{aligned}$$

Since a protein may have about 100 amino acids, and each amino acid has a volume of about 100 \AA^3 , the volume of a protein is about 10^4 \AA^3 . Hence Δv is a small change.

9. Clusters.

Sometimes isolated molecules of type A can be in a two-state equilibrium with a cluster of m monomers, $mA \xrightarrow{K} A_m$, where A_m represents an m -mer cluster.

- At equilibrium, what is the relationship between μ_1 , the chemical potential of the monomer, and μ_m , the chemical potential of A in the cluster?
- Express the equilibrium constant K in terms of the partition functions.

(a) Use Equation (13.16) with $a = m$, $b = 0$, $c = 1$ to get $\mu_m = m\mu_1$

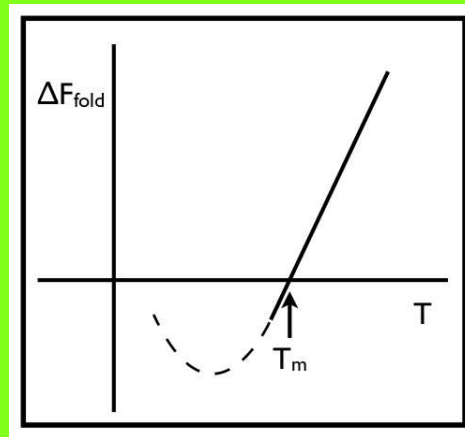
(b) Equation (13.19) gives $K = \left(\frac{q_m}{q_1^m} \right) e^{-\Delta\epsilon_0/kT}$

10. Two-state protein folding model.

In Example 8.2, we considered a two-state model of proteins: the folded state has energy $-\epsilon_0$ (where $\epsilon_0 > 0$) and the unfolded state has $\gamma = 4$ open conformations. The partition function is

$$q = 4 + e^{\frac{\epsilon_0}{kT}}.$$

- Write an expression for the equilibrium constant for folding, $K_f = (\text{population}_{\text{folded}})/(\text{population}_{\text{unfolded}})$ in terms of ϵ_0 and temperature T .
- Using the van't Hoff expression, $(\partial \ln K)/(\partial(1/T))$, derive the enthalpy of folding, ΔH_f , for this model.
- What is the free energy of folding vs. temperature T , $\Delta F_f(T) = F_{\text{folded}} - F_{\text{unfolded}}$?
- This model predicts that $\Delta F_{\text{fold}}(T)$ is a linearly increasing function of T . This is often a good approximation near the denaturation midpoint, T_m .



For myoglobin, which has about 150 amino acids, the slope is 5 kcal/(mol · 10° C) at $T_m = 70^\circ \text{C}$. If instead of choosing $\gamma = 4$, as in our simple model, you chose γ to fit the experimental slope in the figure, what value of γ is needed?

- Since the q 's cancel, $K_f = \frac{e^{\frac{\epsilon_0}{kT}}}{4}$
- $$\frac{\partial \ln K}{\partial(\frac{1}{T})} = -\frac{\Delta H}{K}$$

$$\frac{\partial(\frac{1}{T})}{\partial T} = -\frac{1}{T^2} \implies \frac{\partial \ln K}{\partial T} = \frac{\Delta H}{KT^2}$$

$$K = \frac{1}{4}e^{\frac{\epsilon_0}{kT}} \implies \ln K = \ln(\frac{1}{4}) + \ln(e^{\frac{\epsilon_0}{kT}}) = \ln(\frac{1}{4}) + \frac{\epsilon_0}{kT}$$

$$\begin{aligned} \implies \frac{\partial [\ln(\frac{1}{4}) + \frac{\epsilon_0}{kT}]}{\partial T} &= \frac{\Delta H}{KT^2} \implies -\frac{\epsilon_0}{kT^2} = \frac{\Delta H}{KT^2} \\ \implies \Delta H_f &= -\epsilon_0 \end{aligned}$$

(c) $\Delta F = -kT \ln(K_f)$
 $\Delta F = -kT \ln(\frac{1}{4} e^{\frac{\epsilon_0}{kT}}) = -kT [\ln(\frac{1}{4}) + \ln(e^{\frac{\epsilon_0}{kT}})]$
 $\Delta F = kT \ln(4) - \frac{kT \epsilon_0}{kT}$
 $\implies \Delta F = kT \ln(4) - \epsilon_0$

OR

$$\begin{aligned} \Delta F &= \Delta F_f - \Delta F_{un} \\ F_f &= U_f - TS_f = -\epsilon_0 - Tk \ln(1) \\ F_{un} &= U_{un} - TS_{un} = 0 - Tk \ln(4) \\ \implies \Delta F &= -\epsilon_0 + kT \ln(4) \end{aligned}$$

(d) $\frac{\partial \Delta F}{\partial T} = k \ln(\gamma) = \frac{5000 \text{ cal}}{10^\circ \text{C} \cdot \text{mol}} = \frac{500 \text{ cal}}{\text{K} \cdot \text{mol}} = R \ln(\gamma)$
 $\frac{500 \text{ cal}}{\text{K} \cdot \text{mol}} \frac{\text{mol} \cdot \text{K}}{1.987 \text{ cal}} = \ln(\gamma) = 251.6$
 $\implies \gamma = e^{251.6} = 1.81 \cdot 10^{109}$

Chapter 14

Phase Equilibria

1. Applying the Clausius–Clapeyron equation.

- (a) The vapor pressure of water is 23 mm Hg at $T = 300$ K, and 760 mm Hg at $T = 373$ K. Calculate the enthalpy of vaporization, Δh_{vap} .
- (b) Assuming that each water has $z = 4$ nearest neighbors, calculate the interaction energy, w_{AA} .

$$\begin{aligned}
 \text{(a)} \quad \ln \left(\frac{p_2}{p_1} \right) &= -\frac{\Delta h_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \\
 \Rightarrow \frac{\ln \left(\frac{760}{23} \right)}{\left(\frac{1}{373} - \frac{1}{300} \right)} \left(1.987 \frac{\text{cal}}{\text{mol}} \right) &= -\Delta h_{\text{vap}} \\
 \Rightarrow \Delta h_{\text{vap}} &= 10.653 \frac{\text{kcal}}{\text{mol}}
 \end{aligned}$$

(b) Since

$$\begin{aligned}
 -\frac{zw}{2} &= \Delta h_{\text{vap}}, \\
 w &= -\frac{\Delta h_{\text{vap}}}{2} \approx -5.3 \frac{\text{kcal}}{\text{mol}}.
 \end{aligned}$$

2. How does surface tension depend on temperature?

If the surface tension of a pure liquid is due entirely to energy (and no entropy), then will the surface tension *increase*, *decrease*, or *not change* with increasing temperature?

The surface tension will *not change* with increasing temperature. $\gamma = -\frac{w}{2a}$ is independent of T if w is independent of T .

3. Why do spray cans get cold?

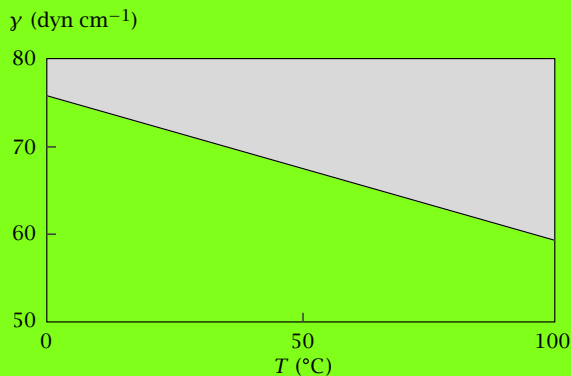
Explain why an aerosol spray can gets cold when you spray the contents.

The contents of a spray can are under high pressure. Pushing the button opens the systems to the atmosphere, reducing the pressure below the vapor pressure of the fluid. This causes the fluid to vaporize. Vaporization absorbs heat from the can, causing it to become cold.

4. The surface tension of water.

The surface tension of water $\gamma(T)$ decreases with temperature as shown in the figure below.

- (a) As a first-order approximation, estimate the water–water pair attraction energy w_{AA} , assuming that the interaction is temperature independent.
- (b) Explain the basis for this attraction.
- (c) Explain why γ decreases with T .



Surface tension of water versus temperature. Source: drawn from data in *CRC Handbook of Chemistry and Physics*, 47th edition, RC Weast, editor, The Chemical Rubber Co, Cleveland, 1962.

(a) From the lattice model of surface tension

$$\gamma = -\frac{w_{AA}}{2a} \quad \text{so} \quad w_{AA} = -2a\gamma$$

Assume the area of a water molecule is about $a = 5 \text{ \AA}^2$, and take a value for γ , say $\gamma = 70 \text{ dynes/cm}$, then

$$\begin{aligned} w_{AA} &\approx -2(5\text{\AA}^2) \left(70 \frac{\text{g}}{\text{s}^2}\right) \left(\frac{1 \text{ J s}^2}{10^7 \text{ g cm}^2}\right) \left(\frac{1 \text{ cm}}{10^8 \text{ \AA}}\right)^2 \\ &\quad \times \left(6.022 \times 10^{23} \frac{\text{molecules}}{\text{mole}}\right) \\ &\approx -4.214 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

(b) Hydrogen bonds and van der Waals attractions.

(c) One simple explanation is that hydrogen bonds in water are broken as temperature increases, which weakens the water–water attractions and thus the surface tension.

5. Applying the Clausius–Clapeyron equation again.

Suppose you want to add a perfuming agent to a liquid aerosol spray. You want its vapor pressure to double if the temperature increases from 25° C to 35° C . Calculate the pair interaction energy that this agent should have in the pure liquid state. Assume that the number of nearest–neighbor molecules in the liquid is $z = 6$.

The vapor pressure is given by

$$p = p_0 \exp\left(\frac{zw}{2RT}\right)$$

We want

$$\frac{p_2}{p_1} = \exp\left(\frac{zw}{2R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}\right) = 2$$

Using $z = 6$, $R = 2 \text{ cal/mol K}$, we have

$$\begin{aligned}\frac{zw}{2R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) &= \ln 2 \\ w &= \frac{2R \ln 2}{z \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \\ &= \frac{2(2 \frac{\text{cal}}{\text{mol K}}) \ln 2}{6 \left(\frac{1}{308\text{K}} - \frac{1}{298\text{K}} \right)} \\ w &= -4.24 \frac{\text{kcal}}{\text{mol}}\end{aligned}$$

6. How does the boiling temperature depend on the enthalpy of vaporization?

A fluid has a boiling temperature $T = 300 \text{ K}$ at $p = 1 \text{ atm}$; $\Delta h_{\text{vap}} = 10 \text{ kcal mol}^{-1}$. Suppose you make a molecular modification of the fluid that adds a hydrogen bond so that the new enthalpy is $\Delta h_{\text{vap}} = 15 \text{ kcal mol}^{-1}$ at $p = 1 \text{ atm}$. What is the new boiling temperature?

$$\begin{aligned}\frac{p}{p_0} &= \exp \left(\frac{-\Delta h_{\text{vap}2}}{RT_2} \right) \\ \text{and } \frac{p}{p_0} &= \exp \left(\frac{-\Delta h_{\text{vap}1}}{RT_1} \right) \\ \implies \exp \left(\frac{-\Delta h_{\text{vap}2}}{RT_2} \right) &= \exp \left(\frac{-\Delta h_{\text{vap}1}}{RT_1} \right) \\ \implies \frac{\Delta h_{\text{vap}2}}{RT_2} &= \frac{\Delta h_{\text{vap}1}}{RT_1} \\ \implies T_2 &= T_1 \left(\frac{\Delta h_{\text{vap}2}}{\Delta h_{\text{vap}1}} \right) \\ &= (300 \text{ K}) \left(\frac{15 \text{ kcal/mol}}{10 \text{ kcal/mol}} \right) \\ &= 450 \text{ K}\end{aligned}$$

7. Trouton's Rule.

- (a) Using Table 14.1, show that the entropy of vaporization, $\Delta s_{\text{vap}} = \Delta h_{\text{vap}}/T_b$, is relatively constant for a broad range of different substances. Δh_{vap} is the enthalpy of vaporization and T_b is the boiling temperature. This is called Trouton's rule.
- (b) Why are the values of Δs_{vap} for water and CO_2 in Table 14.1 larger than for other substances?

(a) Here are some examples from Table 14.1:

$$\begin{array}{lll} \text{C}_6\text{H}_6 & \Delta S & = \frac{30,800 \text{ J/mol}}{353 \text{ K}} = 87.5 \frac{\text{J}}{\text{K mol}} \\ \text{C}_2\text{H}_6 & \Delta S & = \frac{14,700 \text{ J/mol}}{184.55 \text{ K}} = 79.6 \frac{\text{J}}{\text{K mol}} \\ \text{H}_2\text{S} & \Delta S & = \frac{18,673 \text{ J/mol}}{212.8 \text{ K}} = 88.1 \frac{\text{J}}{\text{K mol}} \\ \text{Ar} & \Delta S & = \frac{6,506 \text{ J/mol}}{87.29 \text{ K}} = 74.5 \frac{\text{J}}{\text{K mol}} \\ \text{Na} & \Delta S & = \frac{98,010 \text{ J/mol}}{1156 \text{ K}} = 84.7 \frac{\text{J}}{\text{K mol}} \end{array}$$

Trouton's rule says that the typical ΔS_{vap} is about 85 J/mol.

$$\begin{array}{lll} \text{(b)} \quad \text{H}_2\text{O} & \Delta S & = \frac{40,656 \text{ J/mol}}{373.15 \text{ K}} = 108.95 \frac{\text{J}}{\text{K mol}} \\ & \text{CO}_2 & \Delta S = \frac{25,230 \text{ J/mol}}{194.64 \text{ K}} = 129.62 \frac{\text{J}}{\text{K mol}} \end{array}$$

The rationale is that water is more ordered in its liquid state than simpler materials. The value for CO_2 is for sublimation from the crystal state, which is more ordered than a typical liquid.

8. Sublimation of graphite.

The heat of sublimation of graphite is $\Delta h_{\text{sub}} = 716.7 \text{ kJ mol}^{-1}$. Use this number to estimate the strength of a carbon-carbon bond.

Equation (15.24) applies to sublimation as well as to vaporization, so

$$\Delta h_{\text{sub}} = -\frac{zw_{AA}}{2}$$

In graphite, carbon is in the sp^2 hybridization state, with three bonds and a delocalized π bond. For simplicity, we take $z = 4$ neighbors, so

$$w_{AA} = -\frac{\Delta h_{\text{sub}}}{2} = -358.35 \text{ kJ/mol} = -85.6 \text{ kcal/mol}$$

The experimental value of a C-C single bond is -342 kJ/mol , but it can typically vary from about -300 to -400 kJ/mol depending on neighboring bond substituent effects.

9. Surface tension of mercury.

The surface tension of water is 72 ergs cm^{-2} and of liquid mercury is 487 ergs cm^{-2} . If a water-water attraction is about 5 kcal-mol^{-1} , what is the mercury-mercury attraction?

$$\frac{w_{AA_2}}{w_{AA_1}} = \frac{\gamma_2}{\gamma_1}$$
$$\Rightarrow w_{AA_{Hg}} = \left(\frac{487}{72}\right)(5 \frac{\text{kcal}}{\text{mol}}) = 33 \frac{\text{kcal}}{\text{mol}}$$

10. Squeezing ice.

Use the Clapeyron relation to compute the pressure that is required to lower the melting temperature of ice by 10 K . For water, $\Delta h = 6.008 \text{ kJ-mol}^{-1}$ and $\Delta v = -1.64 \text{ cm}^3\text{-mol}^{-1}$.

$$\int_{P_1}^{P_2} dP = \frac{\Delta h}{\Delta v} \int_{T_1}^{T_2} \frac{dT}{T}$$
$$P_2 = P_1 + \frac{\Delta h}{\Delta v} \ln\left(\frac{T_2}{T_1}\right)$$

The melting temperature of water at 1 atm is 273.15 K .

$$P_2 = 1.013 \cdot 10^5 \text{ Pa} + \frac{6.008 \cdot 10^3 \text{ J}}{-1.64 \cdot 10^{-6} \text{ m}^3} \ln\left(\frac{263.15}{273.15}\right)$$

$$P_2 = 1.366 \cdot 10^8 \text{ Pa} \left(\frac{1 \text{ atm}}{1.013 \cdot 10^5 \text{ Pa}}\right) = 1348 \text{ atm} = 0.137 \frac{\text{kJ}}{\text{cm}^3}$$

Chapter 15

Solutions and Mixtures

1. Ternary lattice mixtures.

Consider a lattice model liquid mixture of three species of spherical particles, A , B , and C . As with binary mixtures, assume that all $N = n_A + n_B + n_C$ sites are filled.

- (a) Write an expression for the entropy of mixing.
- (b) Using the Bragg–Williams approximation, write an expression for the energy of mixing U in terms of the binary interaction parameters χ .
- (c) Write an expression for the chemical potential μ_A of A .

(a) $W = \frac{N!}{n_A!n_B!n_C!}$. Use Stirling's approximation $\ln x! \approx \left(\frac{x}{e}\right)^x$ to get

$$\begin{aligned} \frac{S}{Nk} &= \frac{1}{N} \ln W \\ &= -x_A \ln x_A - x_B \ln x_B - x_C \ln x_C, \end{aligned}$$

where $x_A = n_A/N$, $x_B = n_B/N$, $x_C = n_C/N$.

(b) $U = m_{AA}w_{AA} + m_{BB}w_{BB} + m_{CC}w_{CC} + m_{AB}w_{AB} + m_{AC}w_{AC} + m_{BC}w_{BC}$

Conservation relations:

$$zn_A = 2m_{AA} + m_{AB} + m_{AC}$$

$$zn_B = 2m_{BB} + m_{AB} + m_{BC}$$

$$zn_C = 2m_{CC} + m_{AC} + m_{BC}$$

so we have:

$$\begin{aligned} m_{AA} &= \frac{zn_A - m_{AB} - m_{AC}}{2} \\ m_{BB} &= \frac{zn_B - m_{AB} - m_{BC}}{2} \\ m_{CC} &= \frac{zn_C - m_{AC} - m_{BC}}{2} \end{aligned}$$

Substituting into the expression for U and rearranging terms, we get:

$$\begin{aligned} U &= \frac{zw_{AA}}{2}n_A + \frac{zw_{BB}}{2}n_B + \frac{zw_{CC}}{2}n_C + m_{AB} \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right) \\ &\quad + m_{AC} \left(w_{AC} - \frac{w_{AA} + w_{CC}}{2} \right) + m_{BC} \left(w_{BC} - \frac{w_{BB} + w_{CC}}{2} \right) \end{aligned}$$

Defining χ parameters and using the Bragg–Williams approximation gives

$$\begin{aligned} \frac{U}{NkT} &= \frac{zw_{AA}}{2kT} \frac{n_A}{N} + \frac{zw_{BB}}{2kT} \frac{n_B}{N} + \frac{zw_{CC}}{2kT} \frac{n_C}{N} + \frac{n_A n_B}{N^2} \chi_{AB} + \frac{n_B n_C}{N^2} \chi_{BC} \\ &\quad + \frac{n_A n_C}{N^2} \chi_{AC} \\ &= \frac{zw_{AA}}{2kT} x_A + \frac{zw_{BB}}{2kT} x_B + \frac{zw_{CC}}{2kT} x_C + \chi_{AB} x_A x_B \\ &\quad + \chi_{BC} x_B x_C + \chi_{AC} x_A x_C \end{aligned}$$

so

$$\frac{\Delta U_{\text{mix}}}{NkT} = \chi_{AB} x_A x_B + \chi_{BC} x_B x_C + \chi_{AC} x_A x_C$$

(c) From the definition of chemical potential,

$$\frac{\mu_A}{kT} = \left. \frac{\partial \left(\frac{F}{kT} \right)}{\partial n_A} \right|_{n_B, n_C}$$

We want to hold n_B and n_C constant, but not N , so write in terms of n_A , n_B , and n_C only:

$$\frac{F}{kT} = \frac{U - TS}{kT} = \frac{zw_{AA}}{2kT} n_A + \frac{zw_{BB}}{2kT} n_B + \frac{zw_{CC}}{2kT} n_C + \frac{n_A n_B}{(n_A + n_B + n_C)} \chi_{AB}$$

$$\begin{aligned}
& + \frac{n_A n_C}{(n_A + n_B + n_C)} \chi_{AC} + \frac{n_B n_C}{(n_A + n_B + n_C)} \chi_{BC} \\
& - n_A \ln \left(\frac{n_A + n_B + n_C}{n_A} \right) - n_B \ln \left(\frac{n_A + n_B + n_C}{n_B} \right) \\
& - n_C \ln \left(\frac{n_A + n_B + n_C}{n_C} \right)
\end{aligned}$$

so

$$\begin{aligned}
\frac{\mu_A}{kT} &= \frac{z w_{AA}}{2kT} + \chi_{AB} \left(\frac{N n_B - n_A n_B \cdot 1}{N^2} \right) + \chi_{AC} \left(\frac{N n_C - n_A n_C \cdot 1}{N^2} \right) + \ln x_A \\
&\quad - n_A(x_A) \left(\frac{n_A \cdot 1 - N \cdot 1}{n_A^2} \right) - n_B(x_B) \left(\frac{1}{n_B} \right) - n_C(x_C) \left(\frac{1}{n_C} \right) \\
&= \frac{z w_{AA}}{2kT} + \chi_{AB} x_B (1 - x_A) + \chi_{AC} x_C (1 - x_A) + \ln x_A - x_A \left(1 - \frac{1}{x_A} \right) - x_B - x_C \\
&= \frac{z w_{AA}}{2kT} + \chi_{AB} x_B (x_B + x_C) + \chi_{AC} x_C (x_B + x_C) + \ln x_A - x_A + 1 - x_B - x_C \\
&= \frac{z w_{AA}}{2kT} + \chi_{AB} x_B (x_B + x_C) + \chi_{AC} x_C (x_B + x_C) + \ln x_A
\end{aligned}$$

2. Enthalpy of mixing.

For a mixture of benzene and *n*-heptane having equal mole fractions, $x = 1/2$, and temperature $T = 300$ K, the enthalpy of mixing is $\Delta H_{\text{mix}} = 220 \text{ cal mol}^{-1}$. Compute χ_{AB} .

$$\begin{aligned}
\Delta H_{\text{mix}} &\approx \Delta U_{\text{mix}} = x(1-x)RT\chi_{AB} \\
\text{so } \chi_{AB} &\approx \frac{4\Delta H_{\text{mix}}}{RT} = \frac{(4) \left(220 \frac{\text{cal}}{\text{mol}} \right)}{\left(1.987 \frac{\text{cal}}{\text{K mol}} \right) (300 \text{ K})} \\
&= 1.48
\end{aligned}$$

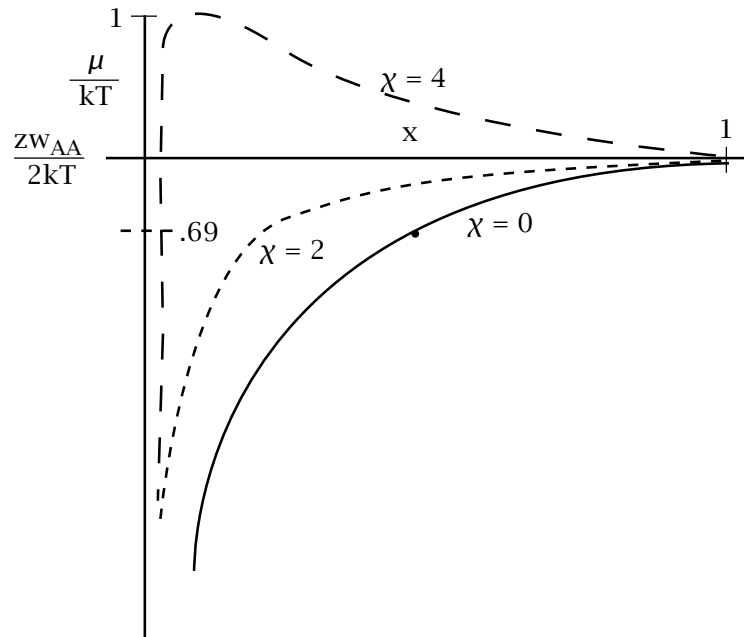
3. Plot $\mu(x)$.

Plot the chemical potential versus x for:

- (a) $\chi_{AB} = 0$,
- (b) $\chi_{AB} = 2$,
- (c) $\chi_{AB} = 4$.

Equation (15.15) gives

$$\frac{\mu}{kT} = \frac{zw_{AA}}{2kT} + \ln x + \chi_{AB}(1-x)^2$$



4. Limit of $x \ln x$ terms in mixing entropies and free energies.

What is the value of $x \ln x$ as $x \rightarrow 0$?

As $x \rightarrow 0$, $x \ln x \rightarrow 0$. More specifically,

$$\lim_{x \rightarrow 0} \frac{\ln x}{\frac{1}{x}} = \lim_{x \rightarrow 0} \frac{\frac{1}{x}}{-\frac{1}{x^2}} = \lim_{x \rightarrow 0} (-x) = 0,$$

using l'Hôpital's rule. This rule says that the limit ($x \rightarrow 0$) of the ratio of functions $f(x)/g(x)$ equals the limit of their derivatives, $f'(x)/g'(x)$.

5. Hydrophobic entropy.

The entropy of dissolving benzene in water at high dilution is approximately $14 \text{ cal mol}^{-1} \text{ K}^{-1}$ at $T = 15^\circ \text{C}$.

- (a) How does this compare with the mixing entropy?
- (b) Speculate on the origin of this entropy.

- (a) The maximum possible mixing entropy occurs for $x = 0.5$, where

$$\begin{aligned} \frac{S}{Rn} &= -2(0.5 \ln 0.5) \\ &= -\ln 0.5 = -0.69, \end{aligned}$$

so

$$\begin{aligned} \frac{S}{n} &= (-0.69)(1.987 \text{ cal/mol K}) \\ &= -1.37 \text{ cal/mol K}. \end{aligned}$$

The mixing entropy is much smaller than the hydrophobic entropy.

- (b) The hydrophobic entropy involves rotational entropy in the waters that surround the solute, which is not taken into account in the mixing entropy.

6. Solubility parameters.

The quantity χ_{AB} describes AB interactions relative to AA and BB interactions. If instead of a 2-component mixture, you had a mixture of N different species A, B, \dots , then, to obtain the pairwise quantities χ_{ij} for all of them, you would need $\sim N^2$ experiments involving mixtures of all the components $i = 1, 2, \dots, N$ with all the components $j = 1, 2, \dots, N$. However, sometimes this can be much simpler. If all the species are nonpolar, then you can make the approximation $w_{AB} \approx \sqrt{w_{AA}w_{BB}}$ (see Chapter 24). Show how this reduces the necessary number of experiments to only $\sim N$.

$$\chi_{AB} = \frac{z}{kT} \left(w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right).$$

If

$$w_{AB} = \sqrt{w_{AA} w_{BB}},$$

then

$$\chi_{AB} = \frac{z}{kT} \left(\sqrt{w_{AA} w_{BB}} - \frac{w_{AA} + w_{BB}}{2} \right).$$

Let

$$\delta A = \sqrt{\frac{|w_{AA}|}{2}}$$

and

$$\delta B = \sqrt{\frac{|w_{BB}|}{2}},$$

so

$$\chi_{AB} = -\frac{z}{kT} (\delta A - \delta B)^2.$$

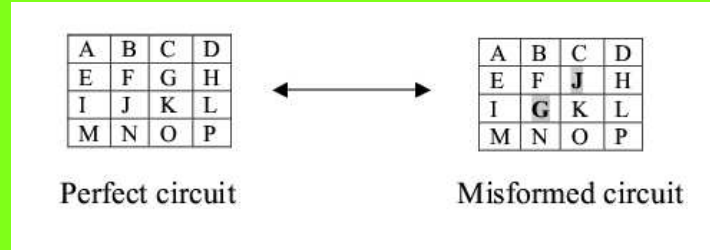
An experiment on pure A gives w_{AA} and δA , and an experiment on pure B gives w_{BB} and δB , so the derived equation gives a way to estimate the interaction parameter χ_{AB} without performing experiments on mixtures.

7. Self-assembly of functional electrical circuits.

G Whitesides and colleagues have pioneered the formation of nano- and meso-scale structures based on the self-assembly of patterned components [Gracias:2000]. Consider a circuit made from the self-assembly of N different building block components. When shaken up together, each component must find its proper place in a two-dimensional square lattice for the circuit to function correctly. Using the figure below, suppose that if the letters are correctly ordered as on the left, each unit interacts pairwise with its neighbor through an interaction energy w_{match} . However, if a letter is surrounded by an incorrect neighbor, it interacts more weakly, with an energy w_{mismatch} . Find the contact energy difference

$$\Delta w = w_{\text{match}} - w_{\text{mismatch}},$$

necessary to ensure that the circuit can be reliably self-assembled. That is, the fraction of working circuits should be higher than δ , where δ is some small value. Ignore shape and surface effects (assume each of the N components makes $z = 4$ contacts) and only consider the equilibrium between a perfectly-formed circuit and all possible misformed circuits in which two components have swapped places. Assume that N is large enough that the defective components are not in contact with one another:



Comparing a correctly self-assembled two-dimensional circuit of parts *vs.* an incorrectly assembled circuit [Gracias:2000]. (left) A perfect Whitesides circuit. (right) One of the possible malformed Whitesides circuits.

Reference: "Forming electrical networks in three dimensions by self-assembly". Gracias DH, Tien J, Breen TL, Hsu C, Whitesides GM. Science. 289(5482):1170-1172. 2000.

Energy of a perfect circuit: $4Nw_{\text{match}}$, $W = 1$

Energy of a perfect circuit: $4(N-2)w_{\text{match}} + 8w_{\text{mismatch}}$, $W = (N-1)(N-2)$

$$Q = e^{-\frac{4Nw_{\text{match}}}{kT}} + (N-1)(N-2)e^{-\frac{4(N-2)w_{\text{match}} + 8w_{\text{mismatch}}}{kT}}$$

We want the probability of a perfectly formed circuit to be greater than δ :

$$\delta < p_{\text{match}} = \frac{e^{-\frac{4Nw_{\text{match}}}{kT}}}{e^{-\frac{4Nw_{\text{match}}}{kT}} + (N-1)(N-2)e^{-\frac{4(N-2)w_{\text{match}} + 8w_{\text{mismatch}}}{kT}}}$$

$$\frac{1}{\delta} > \frac{1}{p_{\text{match}}} = 1 + (N-1)(N-2)e^{\frac{8}{kT}(w_{\text{match}} - w_{\text{mismatch}})}$$

$$\begin{aligned} \frac{1}{\delta} &> 1 + (N-1)(N-2)e^{\frac{8}{kT}\Delta w} \\ \implies \Delta w &> \frac{kT}{8} \ln\left(\frac{1-\delta}{\delta(N-1)(N-2)}\right) \end{aligned}$$

Chapter 16

Solvation and Transfer of Molecules

1. The mechanism of anesthetic drugs.

Anesthetic drug action is thought to involve the solubility of the anesthetic in the hydrocarbon region of the lipid bilayer of biological membranes. According to the classical ‘Meyer–Overton hypothesis,’ anesthesia occurs whenever the concentration of drug is greater than 0.03 mol kg^{-1} membrane, no matter what the anesthetic.

- (a) For gaseous anesthetics like nitrous oxide or ether, how would you determine what gas pressure of anesthetic to use in the inhalation mix for a patient in order to achieve this membrane concentration?
- (b) Lipid bilayers ‘melt’ from a solid-like state to a liquid-like state. Do you expect introduction of the anesthetic to increase, decrease, or not change the melting temperature? If the melting temperature changes, how would you predict the change?

- (a) As a first approximation, assume that the biomembranes in the body act like a beaker of hydrocarbon, and that the anesthetic gas is in equilibrium with the solution. Henry’s Law tells us the relationship between the vapor pressure and the solute concentration in solution at equilibrium. Therefore we must look up, or measure, the Henry’s Law constant for the specific drug over whatever specific hydrocarbon we consider to be most representative of membranes, and then the required applied pressure will be:

$$p_{\text{appl}} = (k_{\text{drug/oil}}) \left(.03 \frac{\text{moles}}{\text{kg membrane}} \right) (z \text{ kg membrane})$$

- (b) If anesthetics in membranes obey the colligative laws (there is good evidence that they do, at least approximately), then we expect solute to partition predominantly into the liquid phase and thus to reduce the melting temperature. This is observed to be the

case for most anesthetics. The degree to which melting temperature is reduced can be calculated from the usual colligative law equations where the relevant enthalpy of freezing is that of the pure membranes.

2. Divers get the bends.

Divers, returning from deep dives, can get the bends from nitrogen gas bubbles in their blood. Assume that blood is largely water. The Henry's law constant for N_2 in water at $25^\circ C$ is 86,000 atm. The hydrostatic pressure is 1 atm at the surface of a body of water and increases by approximately 1 atm for every 33 feet in depth. Calculate the N_2 solubility in the blood as a function of depth in the water, and explain why the bends occur.

From Henry's Law we can determine the relationship between the vapor pressure over a solution, in this case in the form of the nitrogen gas bubbles over its solution in the bloodstream, $p = kx$, where k is the Henry's Law constant for nitrogen gas in water. The pressure of the gas being breathed D feet deep is $\left(1 + \frac{D}{33 \text{ ft}}\right)$ atm. Nitrogen comprises about 80% of the air, so its partial pressure is $0.80 \left(1 + \frac{D}{33 \text{ ft}}\right)$ atm. Therefore, the mole fraction of the solution which is nitrogen gas is

$$x = \frac{p}{k} = \frac{\left(0.80 \left(1 + \frac{D}{33 \text{ ft}}\right) \text{ atm}\right)}{(86,000 \text{ atm})}.$$

Much more gas would dissolve in the diver's blood at the high pressures deep below the surface than at $p = 1$ atm at the water's surface. Therefore, as the diver rises to the surface, the gas that dissolved deep underwater can no longer remain dissolved and bubbles out of his blood. This causes the physiological problems.

3. Hydrophobic interactions.

Two terms describe the hydrophobic effect: (i) hydrophobic hydration, the process of transferring a hydrophobic solute from the vapor phase into a very dilute solution in which the solvent is water, and (ii) hydrophobic interaction, the process of dimer formation from two identical hydrophobic molecules in a water solvent.

- (a) Using the lattice model chemical potentials, and the solute convention, write the standard state chemical potential differences for each of these processes, assuming that these binary mixtures obey the regular solution theory.
- (b) Describe physically, or in terms of diagrams, the driving forces and how these two processes are similar or different.

- (a) Leaving out factors of the internal partition functions, which we assume do not change in the process, we have for *hydration*:

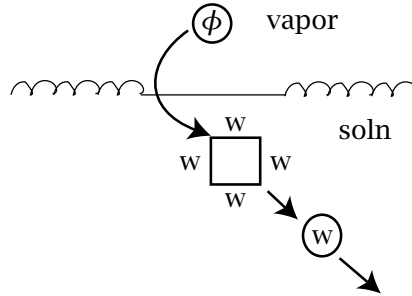
$$\begin{aligned}
\frac{\Delta\mu_{\text{hydration}}^0}{kT} &= \frac{\mu_{\text{liq}}^0 - \mu_{\text{vap}}^0}{kT} = \left(\frac{zw_{\phi\phi}}{2kT} + \chi_{\phi w} - \ln \left(\frac{p}{p_{\phi, \text{int}}^{\circ}} \right) \right) \\
&= \left(\frac{z}{kT} \right) \left(\frac{w_{\phi\phi}}{2} + w_{\phi w} - \frac{w_{\phi\phi} + w_{ww}}{2} \right) - \ln \left(\frac{p}{p_{\phi, \text{int}}^{\circ}} \right) \\
&= \left(\frac{z}{kT} \right) \left(w_{\phi w} - \frac{w_{ww}}{2} \right) - \ln \left(\frac{p}{p_{\phi, \text{int}}^{\circ}} \right)
\end{aligned}$$

where ϕ = solute and w = water.

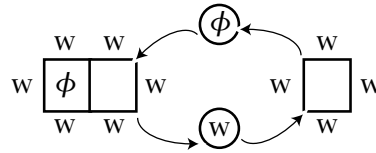
Interaction: From dimerization theory,

$$\begin{aligned}
\frac{\Delta\mu_{\text{interaction}}^0}{kT} &= \frac{\mu_{ww}^0 + \mu_{\phi\phi}^0 - 2\mu_{\phi w}^0}{kT} = -\frac{1}{kT} (2w_{\phi w} - w_{ww} - w_{\phi\phi}kT) \\
&= -\frac{2}{kT} \left(w_{\phi w} - \frac{w_{ww} + w_{\phi\phi}}{2} \right) = -\frac{2}{z} \chi_{\phi w}
\end{aligned}$$

- (b) *Hydration* is favored by stronger ϕw interactions, weaker ww interactions, or higher pressures. $\phi\phi$ interactions do not contribute.



Hydrophobic interaction is favored by weaker ϕw interactions, or stronger ww or $\phi\phi$ interactions. The other difference is that the driving force for hydrophobic interaction is weaker by about $\frac{2}{z}$ relative to hydration.



4. Solutes partition into lipid bilayers.

Robinson Crusoe and his friend Friday are stranded on a desert island with no whiskey, only pure alcohol. Crusoe, an anesthesiologist, realizes that the effect of alcohol, as with other anesthetics, is felt when the alcohol reaches a particular critical concentration, c_0 , in the membranes of neurons. Crusoe and Friday have only a supply of propanol, butanol, and pentanol, and a table of their free energies of transfer for $T = 300$ K.

- (a) A concentration of c_1 of ethanol in water will result in a concentration c_0 in the membrane, which is a hydrocarbon-like environment. Use the table below to predict what concentrations in water of the other alcohols would produce the same degree of anesthesia.

Partitioning quantities in cal mol⁻¹.

	$\mu_w^\circ - \mu_{hc}^\circ$	$h_w^\circ - h_{hc}^\circ$	$s_w^\circ - s_{hc}^\circ$
ethanol	760	-2430	-10.7
propanol	1580	-2420	-13.4
butanol	2400	-2250	-15.6
pentanol	3222	-1870	-17.1

- (b) Mythical cannibals find Crusoe and Friday and throw them into a pot of boiling water. Will the alcohol stay in their membranes and keep them drunk at 100° C?
- (c) Which alcohol has the greatest tendency to partition into the membrane per degree of temperature rise?

- (a) For all 3 alcohols, we need to achieve a concentration of c_0 in the membrane. From the chemical potentials of each, we can get the partition coefficients of each (at $T = 300$ K):

$$\Delta\mu^0 = -RT \ln K \quad K = e^{-\Delta\mu^0/RT}$$

	$\mu_{hc}^0 - \mu_w^0$	$K(hc \leftarrow w)$
eth	-760	3.6
prop	-1580	14.2
but	-2400	56.0
pent	-3222	223

Therefore the relative concentrations needed to achieve this membrane concentration are

$$\text{propanol} \quad \left(\frac{3.6}{14.2} \right) c_1 = 0.25c_1$$

$$\begin{array}{ll} \text{butanol} & \left(\frac{3.6}{56.0}\right) c_1 = 0.064c_1 \\ \text{pentanol} & \left(\frac{3.6}{223}\right) c_1 = 0.016c_1 \end{array}$$

- (b) Using the van't Hoff equation, the temperature dependence of the equilibrium constant is

$$\frac{\partial \ln K_{(hc \leftarrow w)}}{\partial T} = \frac{\Delta h_{(hc \leftarrow w)}}{RT^2} > 0$$

so the alcohol concentration in the membrane increases with temperature.

- (c) It follows that ethanol has the greatest increase in partition coefficient with temperature (2430 > 2420 > 2250).

5. Global warming.

CO₂ in the earth's atmosphere prevents heat from escaping, and is responsible for roughly half of the greenhouse effect, that causes global warming. Would global warming cause a further increase in atmospheric CO₂ through vaporization from the oceans? Assume that the ocean is a two-component solution of water plus CO₂, and that CO₂ is much more volatile than water. Give an algebraic expression for the full temperature dependence of Henry's law constant k_H for the CO₂ in water, that is, derive an equation for $\partial k_H / \partial T$.

Let B represent volatile CO₂, highly dilute in solvent water (A). The vapor pressure of B is

$$\begin{aligned} p_B &= p_{B,\text{int}}^0 x_B \exp \left[\frac{z}{kT} \left(w_{AB} - \frac{w_{AA}}{2} \right) \right] \\ &= p_{B,\text{int}}^0 x_B e^{c/T} \end{aligned}$$

where

$$c = \frac{z}{k} \left(w_{AB} - \frac{w_{AA}}{2} \right).$$

Since

$$\frac{\partial}{\partial T}(e^{c/T}) = -\frac{c}{T^2} e^{c/T},$$

$$\begin{aligned}\frac{\partial p_B}{\partial T} &= -\frac{p_{B,\text{int}}^0 c x_B}{T^2} \exp\left[\frac{c}{T}\right] \\ &= -\frac{k_H x_B c}{T^2}\end{aligned}$$

Since $k_H = p_{B,\text{int}}^0 e^{c/T}$, then we also have

$$\begin{aligned}\frac{\partial k_H}{\partial T} &= -\frac{k_H c}{T^2} \\ \implies \frac{\partial \ln k_H}{\partial T} &= -\frac{c}{T^2} = \frac{\Delta H}{RT^2}\end{aligned}$$

where ΔH is the enthalpy for transferring CO_2 from a water phase to the vapor phase. Since the enthalpy of formation of CO_2 (aq) is -98.69 kcal/mol and of CO_2 (gas) is -94.05 kcal/mol, $\Delta H = 4.64$ kcal/mol and k_H increases with temperature. What complicates the understanding of CO_2 release with temperature is that salts dissolved in the ocean and chemical reactions that form bicarbonates are also involved in the equilibrium.

6. Modelling cavities in liquids.

Assume that you have a spherical cavity of radius r in a liquid. The surface tension of the liquid is γ , in units of energy area⁻¹.

- (a) Write an expression for the energy $\varepsilon(r)$ required to create a cavity of radius r .
- (b) Write an expression for the probability $p(r)$ of finding a cavity of radius r .
- (c) What is the average energy $\langle \varepsilon \rangle$ for cavities in the liquid?
- (d) Write an expression for the average cavity radius.
- (e) If $RT = 600 \text{ cal mol}^{-1}$, and $\gamma = 25 \text{ cal mol}^{-1} \text{Å}^2$, then compute $\langle r \rangle$.

$$(a) \quad e(r) = 4\pi r^2 \gamma$$

$$(b) \quad p(r) = \frac{e^{-e(r)/kT}}{\int_0^\infty e^{-e(r)/kT} dr} = \frac{\exp\left[\frac{-4\pi\gamma r^2}{kT}\right]}{\frac{1}{2}\sqrt{\frac{kT\pi}{4\pi\gamma}}}$$

$$= 4\sqrt{\frac{\gamma}{kT}} \exp\left[\frac{-4\pi\gamma r^2}{kT}\right]$$

$$(c) \quad \text{By equipartition } \langle e \rangle = \frac{1}{2}kT.$$

$$(d) \quad \langle r \rangle = \frac{\int_0^\infty r e^{-4\pi\gamma r^2/kT}}{\int_0^\infty e^{-4\pi\gamma r^2/kT}}$$

$$= \frac{\frac{1}{2}\left(\frac{kT}{4\pi\gamma}\right)}{\frac{1}{2}\left(\frac{\pi kT}{4\pi\gamma}\right)^{1/2}} = \frac{1}{2\pi} \left(\frac{kT}{\gamma}\right)^{1/2}$$

$$(e) \quad \langle r \rangle = \frac{1}{2\pi} \left(\frac{600}{25}\right)^{1/2} = 0.78 \text{Å}$$

7. Sparkling drinks.

CO₂ in water has a Henry's law constant $k_H = 1.25 \times 10^6$ mm Hg. What mole fraction of CO₂ in water will lead to 'bubbling up' and a vapor pressure equal to 1 atm?

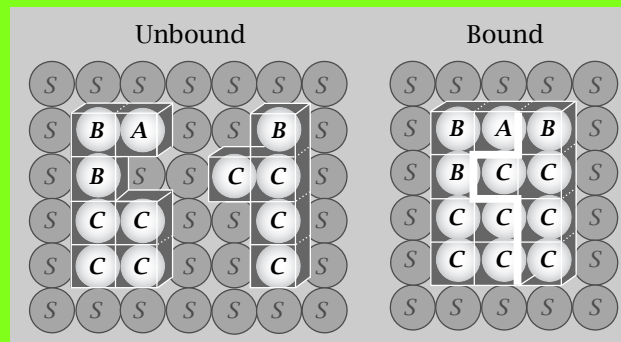
Since the vapor pressure is

$$\begin{aligned}
 p &= k_H x \\
 \text{then } x &= \frac{p}{k_H} = \frac{760 \text{ mm Hg}}{1.25 \times 10^6 \text{ mm Hg}} \\
 \implies x &= 6.08 \times 10^{-4}
 \end{aligned}$$

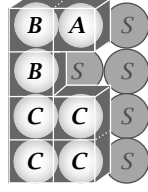
8. Modelling binding sites.

You have a two-dimensional molecular lock and key in solvent s , as shown in the figure below. Different parts of each molecule have different chemical characters, A , B , and C .

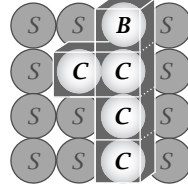
- In terms of the different pair interactions, ($w_{AB}, w_{AC}, w_{AS}, \dots$ etc.) write an expression for the binding constant K (i.e., for association).
- Which type of pair interaction (AB, AC, BC) will dominate the attraction?



Unbound

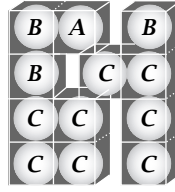


Break 2AS 1BS 3CS
Make 6SS



Break 1BS 5CS
Make 6SS

Bound



Make 1AB 2AC 1BC 3CC

$$(a) \quad K = \left(\frac{q_{\text{bound}}}{q_{\text{lock}} q_{\text{key}}} \right) \exp \left[\frac{1}{kT} (2w_{AS} + 2w_{BS} + 8w_{CS} - w_{AB} - w_{AC} - w_{BC} - 3w_{CC} - 6w_{ss}) \right]$$

- (b) CS and SS interactions will dominate overall because there are the largest number of them. Among AB , AC , BC , it will just depend on which is largest.

9. Oil/water partitioning of drugs.

In the process of partitioning of a drug from oil into water, $\Delta s^\circ = -50 \text{ cal (mol deg)}^{-1}$ and $\Delta h^\circ = 0$ at $T = 300 \text{ K}$.

- (a) What is $\Delta\mu^\circ$ at $T = 300 \text{ K}$?
- (b) What is the partition coefficient from oil to water, $K_{\text{oil}}^{\text{water}}$ at $T = 300 \text{ K}$?
- (c) Assume that Δs° and Δh° are independent of temperature. Calculate K_0^w at $T = 320 \text{ K}$.

$$\begin{aligned} \text{(a)} \quad \Delta\mu^0 &= \Delta h^0 - T\Delta s^0 \\ &= -(300 \text{ K}) \left(-50 \frac{\text{cal}}{\text{mol K}} \right) \\ &= 15.0 \text{ kcal/mol} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta\mu^0 &= -RT \ln K_0^w \\ K_0^w &= \exp \left(-\frac{\Delta\mu^0}{RT} \right) = \exp \left[-\frac{15 \frac{\text{kcal}}{\text{mol}}}{\left(1.987 \frac{\text{cal}}{\text{mol K}} \right) (300 \text{ K})} \right] = 1.18 \times 10^{-11} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \Delta\mu^0(320 \text{ K}) &= \Delta h^0 - T\Delta s^0 \\ &= -(320) \left(-50 \frac{\text{cal}}{\text{mol K}} \right) \\ &= 16.0 \text{ kcal/mol} \\ K_0^w &= \exp \left[-\frac{16 \frac{\text{kcal}}{\text{mol}}}{\left(1.987 \frac{\text{cal}}{\text{mol K}} \right) (320 \text{ K})} \right] = 1.18 \times 10^{-11} \end{aligned}$$

Since $\Delta h^\circ = 0$, K doesn't change with temperature, according to the van't Hoff equation.

10. Another oil/water partitioning problem.

Assume that a drug molecule partitions from water to oil with a partition coefficients $K_1 = 1000$ at $T_1 = 300$ K, and $K_2 = 1400$ at $T_2 = 320$ K.

- (a) Calculate the free energy of transfer, $\Delta\mu^\circ$ at $T_1 = 300$ K.
- (b) Calculate the enthalpy of transfer, Δh° (water to oil).
- (c) Calculate the entropy of transfer, Δs° (water to oil).

$$\begin{aligned} \text{(a)} \quad \Delta\mu_{\text{transfer}}^\circ &= -RT \ln K \\ &= -(1.987 \frac{\text{cal}}{\text{mol deg}}) (300 \text{ K}) \ln 1000 \\ &= -4.118 \frac{\text{kcal}}{\text{mol}} \end{aligned}$$

- (b) Here we assume that Δh° is independent of temperature. Then we use the van't Hoff formula:

$$\begin{aligned} \Delta h^\circ &= -R \frac{(\ln K_2 - \ln K_1)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \\ &= -(1.987 \frac{\text{cal}}{\text{mol deg}}) \frac{\ln 1400 - \ln 1000}{\left(\frac{1}{320 \text{ K}} - \frac{1}{300 \text{ K}}\right)} = 3.21 \frac{\text{kcal}}{\text{mol}} \end{aligned}$$

$$\text{(c)} \quad \Delta s^\circ = \frac{\Delta h^\circ - \Delta\mu^\circ}{T} = \frac{3.21 \frac{\text{kcal}}{\text{mol}} + 4.12 \frac{\text{kcal}}{\text{mol}}}{300 \text{ K}} = 24.4 \frac{\text{cal}}{\text{mol K}}$$

11. Oil/water partitioning of benzene.

You put the solute benzene into a mixture containing the two solvents oil and water. You observe the benzene concentration in water to be $x_w = 2.0 \times 10^{-6}$ M and in oil to be $x_o = 5.08 \times 10^{-3}$ M.

- (a) What is the partition coefficient $K_{\text{water}}^{\text{oil}}$ (from water into oil)?
- (b) What is $\Delta\mu^\circ$ for the transfer of benzene from water into oil at $T = 300$ K?

$$(a) \quad K_w^o = \frac{x_o}{x_w} = \frac{5.08 \times 10^{-3} M}{2.0 \times 10^{-6} M} = 2540$$

$$(b) \quad \begin{aligned} \Delta\mu^o &= -RT \ln K_w^o = - \left(1.987 \frac{\text{cal}}{\text{mol K}} \right) (300 \text{ K}) \ln(2540) \\ &= -4.673 \frac{\text{kcal}}{\text{mol}} \end{aligned}$$

12. Balancing osmotic pressures.

Consider a membrane-enclosed vesicle that contains within it a protein species A that cannot exchange across the membrane. This causes an osmotic flow of water into the cell. Could you reverse the osmotic flow by a sufficient concentration of a different nonexchangeable protein species B in the external medium?

Yes; the osmotic flow could be reversed because at low concentrations each distinguishable species of nonexchangeable component reduces the chemical potential independently of every other species.

13. Vapor pressure of large molecules.

Why do large molecules, such as polymers, proteins, and DNA, have very small vapor pressures?

Large molecules have low vapor pressure because the vapor pressure decreases exponentially with the energy of attraction of the molecule for its neighbors. A large molecule has many such attractive interactions. For example, if the vapor pressure for a “single-lattice-site-solute” is

$$p_A = p_o \exp \left[\frac{zw_{AA}}{2RT} \right]$$

then for a chain of n A -type monomers, the vapor pressure will be

$$p_{\text{chain}} = p'_o \exp \left[\frac{n(z-2)w_{AA}}{2RT} \right]$$

Since $w_{AA} < 0$, if n is large, p_{chain} will be small.

14. Osmosis in plants.

Consider the problem of how plants might lift water from ground level to their leaves. Assume that there is a semipermeable membrane at the roots, with pure water on the outside, and an ideal solution inside a small cylindrical capillary inside the plant. The solute mole fraction inside the capillary is $x = 0.001$. The radius of the capillary is 10^{-2} cm. The gravitational potential energy that must be overcome is mgh , where m is the mass of the solution, and g is the gravitational constant, 980 cm s^{-2} . The density of the solution $= 1 \text{ g cm}^{-3}$. What is the height of the solution at room temperature? Can osmotic pressure account for raising this water?

For the given ideal solution, the osmotic pressure is given by

$$\Delta\mu = \pi v = kT x_{\text{solute}}$$

where v equals the molar volume of solvent (water).

This free energy equals the gravitational potential energy at equilibrium:

$$\Delta\mu = mgh$$

But $mgh = \rho Vgh$ and $V_{\text{cylinder}} = \pi r^2 h$ so

$$\Delta\mu = \rho g \pi r^2 h^2 = \pi v = kT x_{\text{solute}}.$$

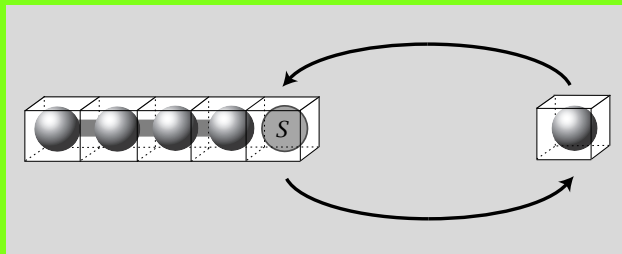
Therefore

$$\begin{aligned} h^2 &= \frac{kT x_{\text{solute}}}{\rho g \pi r^2} \\ h^2 &= \frac{(4.14 \times 10^{-14} \frac{\text{g cm}^2}{\text{s}^2})(0.001)}{(1 \frac{\text{g}}{\text{cm}^3})(980 \frac{\text{cm}}{\text{s}^2})(3.14)(10^{-4} \text{ cm}^2)} \\ \Rightarrow h &\approx 10^{-8} \text{ cm} \end{aligned}$$

Therefore, although osmotic pressure does contribute to water transport inside of trees, other factors, such as transpiration of the water from the leaves, are much more important.

15. Polymerization in solution.

Using the lattice dimerization model (see the figure below), derive the equilibrium constant for creating a chain of m monomers of type A in a solvent s .



The generalization of Equation (16.53) for the association of m monomers is

$$\ln \left[\frac{x_{Am}}{x_A^m} \right] = \left(\frac{m}{z} \right) \chi_{sA} + \ln \left[\frac{q_{AA}}{q_A^m} \right].$$

16. Ethane association in water

The association of ethane molecules in water is accompanied by an enthalpy of $2.5 \text{ kcal mol}^{-1}$ at $T = 25^\circ \text{C}$. Calculate $(\partial \ln K_{\text{assoc}} / \partial T)$ at this temperature. Does the ‘hydrophobic effect’ get stronger or weaker as temperature is increased?

$$\Delta \mu_{\text{assoc}}^o = -RT \ln K_{\text{assoc}} \quad \Rightarrow \quad \ln K_{\text{assoc}} = -\frac{1}{RT} [\Delta h_{\text{assoc}}^o - T \Delta s_{\text{assoc}}^o]$$

assume Δh^o , Δs^o are independent of T ; then

$$\frac{\partial \ln K_{\text{assoc}}}{\partial T} = \frac{\Delta h_{\text{assoc}}^o}{RT^2} = \frac{2500 \frac{\text{cal}}{\text{mol}}}{(1.987 \frac{\text{cal}}{\text{mol K}})(298 \text{ K})^2} = 0.0142 \text{ K}^{-1}$$

As T increases, K_{assoc} increases \Rightarrow hydrophobic effect gets stronger.

17. Freezing point depression by large molecules.

Freezing temperature depression is a useful way of measuring the molecular weights of some molecules. Is it useful for proteins? One g of protein of molecular weight $100,000 \text{ g mol}^{-1}$ is in 1 g of water. Calculate the freezing temperature of the solution.

Freezing temperature depression may be calculated for ideal solutions by

$$T_o - T = \frac{RT_f^2}{\Delta H_{\text{fus}}} x_{\text{solute}}$$

where the mole fraction of solute is given by

$$x_{\text{solute}} \approx \frac{\left(\frac{1 \text{ g solute}}{10^5 \text{ g/mol}} \right)}{\left(\frac{1 \text{ g water}}{18 \text{ g/mol}} \right)} = 1.8 \times 10^{-4}$$

Therefore

$$\begin{aligned} \Delta T &= \frac{(1.987 \text{ cal/mol K})(273.16 \text{ K})^2}{(2350 \text{ cal/mol})} (1.8 \times 10^{-4}) \\ &= 0.0114 \text{ K} \end{aligned}$$

The freezing temperature depression is too small to measure molecular weights of very large molecules.

18. Partitioning into small droplets is opposed by interfacial tension.

When a solute molecule (s) partitions from water (A) into a small oil droplet (B), the droplet will grow larger, creating a larger surface of contact between the droplet and the water. Thus partitioning the solute into the droplet will be opposed by the droplet's interfacial tension with water. Derive an expression to show how much the partition coefficient will be reduced as a function of the interfacial tension and radius of the droplet.

Begin with the Gibbs free energy function, since the process is at constant T and p , but recognize that the droplet surface area a increases if a solute is added, so you need to include

the conjugate pair γa . Therefore $G(T, p, N, a)$ and

$$dG = -SdT + Vdp + \mu_A(s) dN_{SA} + \mu_B(s) dN_{SB} + \gamma da,$$

where N_{SB} is the number of solute (s) molecules in the droplet B and N_{SA} is the number of solute molecules in the external water phase. The constraint is $N_{SA} + N_{SB} = \text{constant}$, so the equilibrium condition (at constant T and p) is

$$[\mu_B(s) - \mu_A(s)] dN_{SB} + \gamma da = 0. \quad (a)$$

Now changes in area a are not independent of changes in N_{SB} because adding a solute increases the volume of the droplet. To find the relationship between dN_{SB} and da first note that the increased volume, dV , of the droplet is

$$dV = v dN_{SB} \quad (b)$$

where v is the volume of a solute molecule. If the droplet is a sphere before and after the uptake of solute, then the area is $A = 4\pi r^2$ and the volume is $V = (4/3)\pi r^3$, where r is the radius. So we have

$$dA = 8\pi r dr$$

and

$$dV = 4\pi r^2 dr$$

so

$$dA = \frac{2}{r} dr \quad (c)$$

Substituting (b) and (c) into (a) gives

$$\left[\mu_B(s) - \mu_A(s) + \frac{2\gamma v}{r} \right] dN_{SB} = 0.$$

Using the lattice model for solute at infinite dilution in both phases gives

$$\ln K_A^B = \ln \left(\frac{x_{SB}}{x_{SA}} \right) = -(\chi_{SB} - \chi_{SA}) - \frac{2\gamma v}{r}.$$

Here are some implications of this expression. (a) As $r \rightarrow \infty$, the partition coefficient approaches the bulk value. (2) As r , the droplet radius, becomes small, solute is increasingly expelled from the droplet. (3) As the solute radius increases or the droplet interfacial tension with water increases, solute is expelled.

19. Alternative description of Henry's Law

Show that an alternative way to express Henry's law of gas solubility is to say that the volume of gas that dissolves in a fixed volume of solution is independent of pressure at a given temperature.

Henry's Law of solubility: $p_a = k_a x_a$. p_a is the vapor pressure of the gas, k_a is Henry's Law constant for the gas in the particular solvent, and x_a is the mole fraction of gas in solution.

The essence of this problem is in the conversion from mole fraction of gas to volume fraction:

$$\begin{aligned} \phi_a &= \text{vol fraction} = \frac{V_{\text{gas}}}{V_{\text{solution}}} \approx \frac{V_{\text{gas}}}{V_{\text{solvent}}} \\ x_a &= \phi_a \left(\frac{\frac{\text{moles}}{V} \text{ gas}}{\frac{\text{moles}}{V} \text{ solvent}} \right) \end{aligned}$$

Assume the gas is ideal. Then

$$\frac{\text{moles gas}}{\text{vol. gas}} = \frac{n}{V} = \frac{p_a}{RT}$$

For the solvent

$$\frac{\text{moles solvent}}{\text{vol. solvent}} = \frac{1}{v}$$

where v is the molar volume of the solvent. Therefore

$$x_a = \phi_a \left(\frac{\frac{p_a}{RT}}{\frac{1}{v}} \right) = \phi_a \left(\frac{p_a v}{RT} \right)$$

Substitute into Henry's Law:

$$\begin{aligned} p_a &= k_a \phi_a \left(\frac{p_a v}{RT} \right) \\ \text{so } \phi_a &= \frac{RT}{k_a v}, \end{aligned}$$

i.e., the *volume* fraction of gas dissolved is independent of pressure at constant temperature.

20. Benzene transfer into water.

At $T = 25^\circ \text{C}$, benzene dissolves in water up to a mole fraction of 4.07×10^{-4} (its solubility limit).

- Compute $\Delta\mu^\circ$ for transferring benzene to water.
- Compute $\chi_{\text{benzene,water}}$.
- Write an expression for the temperature dependence of $\Delta\mu^\circ$ as a function of Δh° , Δs° , the molar enthalpy and entropy at 25°C , and ΔC_p .
- Using the expression you wrote for (c), calculate $\Delta\mu^\circ$ for transferring benzene to water at $T = 100^\circ \text{C}$, if $\Delta h^\circ = 2 \text{ kJ mol}^{-1}$, $\Delta s^\circ = -58 \text{ J mol K}^{-1}$, and $\Delta C_p = 225 \text{ J mol K}^{-1}$.

$$\begin{aligned} \text{(a)} \quad \Delta\mu^\circ &= -kT \ln x = - \left(1.987 \frac{\text{cal}}{\text{mol K}} \right) (298 \text{ K}) \ln(4.07 \times 10^{-4}) \\ &= -4.62 \frac{\text{kcal}}{\text{mol}} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \chi_{AB} &= -\ln x = -\ln(4.07 \times 10^{-4}) \\ &= 7.81 \end{aligned}$$

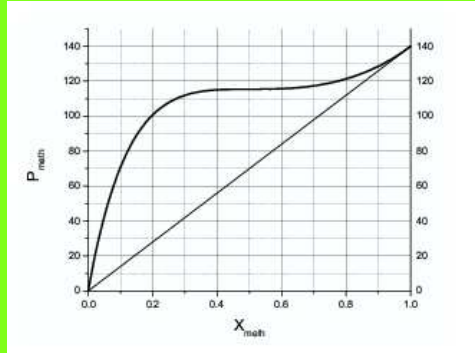
(c) Assuming that Δh° , Δs° , and ΔC_p are all temperature-independent, then

$$\begin{aligned}\Delta\mu^\circ &= \Delta h - T\Delta s \\ &= \Delta h^\circ - T\Delta s^\circ + \Delta C_p(T - 298 \text{ K}) - T\Delta C_p \ln\left(\frac{T}{298 \text{ K}}\right)\end{aligned}$$

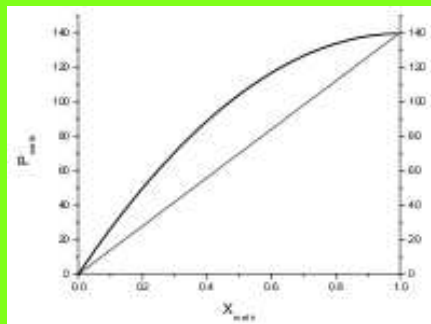
$$\begin{aligned}\text{(d)} \quad \Delta\mu^\circ &= \left(2 \frac{\text{kJ}}{\text{mol}}\right) + (373 \text{ K}) \left(58 \frac{\text{J}}{\text{mol K}}\right) \\ &\quad + \left(225 \frac{\text{J}}{\text{mol K}}\right) (75 \text{ K}) - (373 \text{ K}) \left(225 \frac{\text{J}}{\text{mol K}}\right) \ln\left(\frac{373}{298}\right) \\ &= (2000 + 21,634 + 16,875 - 18,840) \frac{\text{J}}{\text{mol}} \\ &= 21.7 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

21. Raoult's Law for methanol-water mixtures.

The figure below plots the vapor pressure, in mm Hg, versus composition for methanol in a binary solution with water at 300 K. Raoult's Law behavior is indicated by the straight line.



- Using the lattice model, calculate the contact energy w for methanol. To simplify, neglect the internal degrees of freedom for methanol, and assume a lattice with $z = 6$.
- From the graph, estimate the value of the exchange parameter, χ , for the methanol-water mixture.
- Using the lattice model expression for the activity coefficient, show that p_{meth} approaches P_{meth}^* (the equilibrium, vapor pressure above pure methanol) as with the same slope as Raoult's law. That is, the plot for P_{meth} should resemble the figure above, and not the figure shown below.



- From the graph, it is clear that for pure methanol ($\chi_{\text{meth}} = 1$), the equilibrium vapor pressure is 140 mm Hg. This can be used with the equation from the text just after eq. 15.3:

$$P^* = P_{\text{int}}^o e^{\frac{zw}{2kT}}, \text{ where eq. 10.49 gives } P_{\text{int}}^o = kT \left(\frac{2\pi mkT}{h^2} \right)^{3/2}$$

Note that in calculating the internal pressure term you do not have to include the internal degrees of freedom; but you still need to include the translational degrees of

freedom for the P_{int}^o term. Solving this for w :

$$w = \frac{2kT}{z} \ln\left(\frac{P^*}{P_{int}^o}\right) = \frac{2kT}{z} \ln\left(\frac{P^*}{kT} \left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right)$$

$$w = \frac{2 \cdot 1.38 \cdot 10^{-23} \cdot 300}{6} \ln\left(\frac{\frac{140}{760} \cdot 1.013 \cdot 10^5}{1.38 \cdot 10^{-23} \cdot 300} \left(\frac{6.626^2 \cdot 10^{-68}}{2 \cdot 3.14 \cdot 32 \cdot 1.78 \cdot 10^{-27} \cdot 1.38 \cdot 10^{-23} \cdot 300}\right)^{3/2}\right)$$

$$w = -2.427 \cdot 10^{-20} \frac{\text{J}}{\text{molecule}} = -14.6 \frac{\text{kJ}}{\text{mol}}$$

- (b) At $X_{meth} = 0.2$, for example, $P_{meth} = 100$ mm Hg, while Raoult's Law gives $P_{meth} = P_{meth}^* X_{meth} = 28$ mm Hg. The activity coefficient, on the solvent convention, γ , is $\frac{P_{meth}}{P_{meth}^* X_{meth}} = \frac{100}{28} = 3.75$.

This can be related to the exchange parameter, χ , by $\gamma = e^{\chi(1-X_{meth})^2}$
 $\Rightarrow \chi = \frac{\ln \gamma}{(1-X_{meth})^2} = \frac{\ln 3.75}{0.64} = 1.99$

- (c) According to the lattice model, we have $P_{meth} = \gamma X_{meth} P_{meth}^*$

$$\Rightarrow \frac{dP_{meth}}{dX_{meth}} = \frac{d\gamma}{dX_{meth}} X_{meth} P_{meth}^* + \gamma \left(\frac{dX_{meth}}{dX_{meth}}\right) P_{meth}^*$$

$$\frac{dP_{meth}}{dX_{meth}} = -(1 - X_{meth}) e^{\chi(1-X_{meth})^2} X_{meth} P_{meth}^* + e^{\chi(1-X_{meth})^2} P_{meth}^*$$

and in the limit as $X_{meth} \rightarrow 1$, $\frac{dP_{meth}}{dX_{meth}} \rightarrow 0 + P_{meth}^* = P_{meth}^*$

This is the same slope as that for Raoult's Law line.

22. Vapor Pressure of Water.

- (a) At a vapor pressure of $p = 0.03$ atm, and a temperature $T = 25^\circ \text{C}$, what is the density of water vapor? Assume an ideal gas.
- (b) What is the corresponding density of liquid water under the same conditions?
- (c) If the vapor pressure of water is 0.03 atm at $T = 25^\circ \text{C}$, and 1 atm at $T = 100^\circ \text{C}$, what is the pairwise interaction energy w_{AA} , if each water molecule has 4 nearest neighbors?

- (a) $PV = nRT$

$$\rho = \frac{n}{V} = \frac{P}{RT} = \frac{0.03 \text{ atm}}{8.206 \cdot 10^{-5} \frac{\text{m}^3 \text{ atm}}{\text{K} \cdot \text{mol}} (300 \text{ K})} \approx 1.22 \frac{\text{mol}}{\text{m}^3}$$

- (b) $\frac{p_B}{p_{B,int}^o} = x_B e^{\frac{z w_{BB}}{2kT}}$

$$x_B = \frac{p_B}{p_{B,int}^o} e^{-\frac{z w_{BB}}{2kT}}, \text{ where } p_B = p_{B,int}^o e^{\frac{z w_{BB}}{2kT}}$$

$$\Rightarrow x_B = \frac{p_{B,int}^o}{p_{B,int}^o} e^{-\frac{z w_{BB}}{2kT}} e^{\frac{z w_{BB}}{2kT}} = 1$$

- (c) $\frac{p_{1A}}{p_{A,int}^o} = e^{\frac{4w_{AA}}{2kT_1}}, \frac{p_{2A}}{p_{A,int}^o} = e^{\frac{4w_{AA}}{2kT_2}}$

Solving for $p_{A,int}^o$ and equating,

$$\begin{aligned} \Rightarrow \frac{p_{1A}}{e^{\frac{4w_{AA}}{2kT_1}}} &= \frac{p_{2A}}{e^{\frac{4w_{AA}}{2kT_2}}} \\ \frac{p_{1A}}{p_{2A}} &= e^{\frac{4w_{AA}}{2k(\frac{1}{T_1} - \frac{1}{T_2})}} \\ \Rightarrow w_{AA} &= \frac{k \ln(\frac{p_{1A}}{p_{2A}})}{2(\frac{1}{T_1} - \frac{1}{T_2})} \end{aligned}$$

23. Osmotic pressure of sucrose.

What is the osmotic pressure of a 0.1 molar solution of sucrose in water at $T = 300$ K?

$$\pi \approx c_A RT = 0.1 \frac{\text{mol}}{\text{L}} (8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}) (300 \text{ K}) (10^3 \frac{\text{L}}{\text{m}^3}) = 249.42 \cdot 10^3 \frac{\text{J}}{\text{m}^3} \approx 2.5 \cdot 10^5 \frac{\text{J}}{\text{m}^3}$$

Chapter 19

Chemical kinetics

1. Isotope substitution experiments can detect hydrogen tunneling.

Isotope substitution experiments can sometimes be used to determine whether hydrogens are cleared from molecules through mechanisms that involve tunnelling. To test this, two isotopes are substituted for hydrogen: (1) deuterium (D, mass = 2) is substituted and the ratio of rate coefficients k_H/k_D is measured, and (2) tritium (T, mass = 3) is substituted and k_H/k_T is measured.

(a) Using the isotope substitution model in this chapter, show that

$$\frac{k_H}{k_T} = \left(\frac{k_H}{k_D} \right)^\alpha.$$

(b) compute the numerical value of α .

You have

$$\frac{k_H}{k_D} = \exp \left[-\frac{h\nu_H}{2kT} \left(\frac{1}{\sqrt{2}} - 1 \right) \right]$$

Similarly

$$\frac{k_H}{k_T} = \exp \left[-\frac{h\nu_H}{2kT} \left(\frac{1}{\sqrt{3}} - 1 \right) \right]$$

$$\text{so } \frac{k_H}{k_T} = \left(\frac{k_H}{k_D} \right)^\alpha$$

$$\text{where } \alpha = \frac{\left(\frac{1}{\sqrt{3}} - 1 \right)}{\left(\frac{1}{\sqrt{2}} - 1 \right)} = \frac{-0.4226}{-0.2929} = 1.443$$

2. Relating stability to activation barriers.

Using the Evans-Polanyi model, with $r_1 = 5$, $r_2 = 15$, $m_1 = 1$, and $m_2 = -2$:

- Compute the activation barriers E_a for three systems having product stabilities $\Delta G = -2 \text{ kcal mol}^{-1}$, -5 kcal mol^{-1} , and -8 kcal mol^{-1} .
- Plot the three points E_a versus ΔG , to show how the activation barrier is related to stability.

- Use Eqn. 19.52:

$$E_a = \left(\frac{m_1}{m_1 - m_2} \right) [\Delta G - m_2(r_2 - r_1)]$$

$$= \left(\frac{1}{3} \right) [\Delta G + 2(10)] = \frac{\Delta G + 20}{3}$$

$$\text{so for } \begin{array}{ll} \Delta G = -2, & E_a = 6 \\ \Delta G = -5, & E_a = 5 \\ \Delta G = -8, & E_a = 4 \end{array}$$

- This shows that the activation barrier decreases linearly with increasing stability of the product: the more stable the product, the faster the reaction.

3. Reduced masses.

Equations (19.40) and (19.41) give the reduced masses for C-H and C-D bonds as $\mu_{CH} \approx m_H$ and $\mu_{CD} \approx 2m_H$. The approximation is based on assuming the mass of carbon is much greater than of H or D. Give the more correct values of these reduced masses if you don't make this assumption.

$$\begin{aligned}\mu_{\text{CH}} &= \frac{m_{\text{C}}m_{\text{H}}}{m_{\text{C}} + m_{\text{H}}} = \frac{12}{13}m_{\text{H}} = 0.923m_{\text{H}} \\ \mu_{\text{CD}} &= \frac{m_{\text{C}}m_{\text{D}}}{m_{\text{C}} + m_{\text{D}}} = \frac{12}{14}(2m_{\text{H}}) = 1.714m_{\text{H}}\end{aligned}$$

4. Classical collision theory.

According to the kinetic theory of gases, the reaction rate k_2 of a sphere of radius r_A with another sphere of radius r_B is

$$k_2 = \pi R^2 \left(\frac{8kT}{\pi\mu_{AB}} \right)^{1/2} e^{-\Delta\epsilon_0^\ddagger/kT},$$

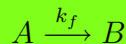
where $R = r_A + r_B$ is the distance of closest approach, μ_{AB} is the reduced mass of the two spheres, and $\Delta\epsilon_0^\ddagger$ is the activation energy. Derive this from transition state theory.

The transition state is an AB dimer having mass $m_A + m_B$ and a rotational partition function with moment of inertia $I = \mu_{AB}R^2$. Using $\mu_{AB} = (m_A m_B)/(m_A + m_B)$ and transition state theory gives

$$\begin{aligned}k_2 &= q_v^\ddagger q_r q_t \\ &= \left(\frac{kT}{h} \right) \left(\frac{8\pi^2 \mu_{AB} R^2 kT}{h^2} \right) \left[\frac{2\pi(m_A + m_B)kT h^{-2}}{(2\pi m_A kT h^{-2})(2\pi m_B kT h^{-2})} \right]^{3/2} e^{-\frac{\Delta\epsilon_0^\ddagger}{kT}} \\ &= \left(\frac{8\pi^2 \mu_{AB} R^2 (kT)^2}{h^3} \right) \left[\frac{h^2}{2\pi kT} \right]^{3/2} \left[\frac{1}{\mu_{AB}} \right]^{3/2} e^{-\frac{\Delta\epsilon_0^\ddagger}{kT}} \\ &= \pi R^2 \left(\frac{8kT}{\pi\mu_{AB}} \right)^{1/2} e^{-\frac{\Delta\epsilon_0^\ddagger}{kT}}\end{aligned}$$

5. The pressure dependence of rate constants.

(a) Show that the pressure dependence of the rate constant k for the reaction



is proportional to an *activation volume* v^\ddagger ,

$$\left(\frac{\partial \ln k_f}{\partial p} \right) = -\frac{(v^\ddagger - v_A)}{kT}.$$

(b) Show that the expression in (a) is consistent with Equation (12.45), $K = k_f/k_r$, where k_r is the rate of the reverse reaction.

(a) Here $k_f = K^\ddagger k^\ddagger$, where K^\ddagger is like an equilibrium constant between the reactant and transition state, and where k^\ddagger depends only on T and not on pressure. Then from Equation (12.45) we get

$$\frac{\partial \ln k_f}{\partial p} = \frac{\partial \ln K^\ddagger}{\partial p} + \frac{\partial \ln k^\ddagger}{\partial p} = -\frac{v^\ddagger - v_A}{kT} + 0$$

where v^\ddagger is the volume of the transition state.

(b) Since $K = \frac{k_f}{k_r}$,

$$\frac{\partial \ln K}{\partial p} = \frac{\partial \ln k_f}{\partial p} - \frac{\partial \ln k_r}{\partial p} = -\frac{v^\ddagger - v_A}{kT} + \frac{v^\ddagger - v_B}{kT} = -\frac{v_B - v_A}{kT}$$

which is what we get in Eqn.12.45.

6. Relating the Arrhenius and activated state parameters.

Derive the relationship of the activation parameter ΔH^\ddagger in Equation (19.19) to the Arrhenius activation energy E_a in Equation (19.4) for a gas-phase reaction.

For the forward reaction, you have the Arrhenius Equation (19.15)

$$\frac{d \ln k_f}{dT} = \frac{E_a}{kT^2} \quad (1)$$

Using the Gibbs–Helmholtz Eqn (13.43) gives

$$\frac{d \ln \overline{K}^\ddagger}{dT} = \frac{\Delta U^\ddagger}{kT^2} \quad (2)$$

(Since \overline{K}^\ddagger has partition functions that depend on V , we are using the (T, V, N) ensemble, so the right side is ΔU^\ddagger rather than ΔH^\ddagger .) Substituting thermodynamic relationships and the ideal gas law into the equation gives

$$\begin{aligned} \frac{d \ln \overline{K}^\ddagger}{dT} &= \frac{\Delta H^\ddagger - p\Delta V^\ddagger}{kT^2} \\ &= \frac{\Delta H^\ddagger - \Delta n^\ddagger kT}{kT^2} \end{aligned} \quad (3)$$

where ΔV^\ddagger is the activation volume and Δn^\ddagger is the stoichiometric change during the reaction. Taking the derivative of Equation (19.28), $k_f = \left(\frac{kT}{h}\right) \overline{K}^\ddagger$, gives

$$\frac{d \ln k_f}{dT} = \frac{1}{T} + \frac{d \ln \overline{K}^\ddagger}{dT} \quad (4)$$

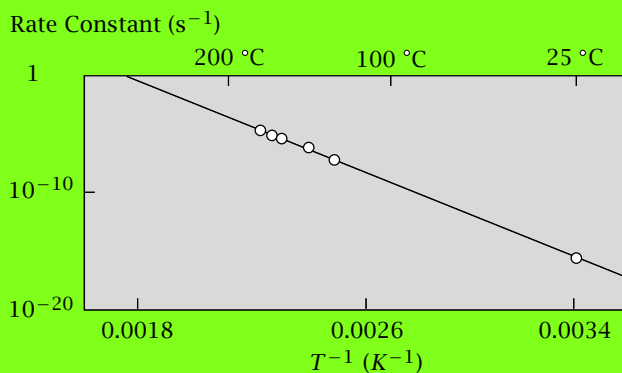
Substitute Equations (1) and (3) into Equation (4) to get

$$\begin{aligned} \frac{E_a}{kT^2} &= \frac{1}{T} + \frac{\Delta H^\ddagger - \Delta n^\ddagger kT}{kT^2} \\ \implies E_a &= \Delta H^\ddagger + kT(1 - \Delta n^\ddagger) \end{aligned}$$

7. Enzymes accelerate chemical reactions.

The figure below shows an Arrhenius plot for the uncatalyzed reaction of 1-methylorotic acid (OMP).

- Estimate ΔH^\ddagger from the figure.
- Estimate ΔS^\ddagger at $T = 300$ K.
- At $T = 25^\circ\text{C}$, the enzyme OMP decarboxylase accelerates this reaction 1.4×10^{17} -fold. How fast is the catalyzed reaction at 25°C ?
- What is the binding constant of the enzyme to the transition state of the reaction at $T = 300$ K?



Source: A Radzicka and R Wolfenden, *Science* **267**, 90–93 (1995).

- (a) Since

$$\frac{k_2}{k_1} = \left(\frac{kT_2/h}{kT_1/h} \right) \exp \left[-\frac{\Delta H^\ddagger}{k} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

you have

$$\ln \frac{k_2}{k_1} = \ln \left(\frac{T_2}{T_1} \right) - \frac{\Delta H^\ddagger}{k} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Take 2 points, such as $(T_1, k_1) = (560 \text{ K}, 1 \text{ s}^{-1})$, $(T_2, k_2) = (294 \text{ K}, 1 \times 10^{-16} \text{ s}^{-1})$. Then

$$\Delta H^\ddagger = \frac{k \left[\ln \left(\frac{T_2}{T_1} \right) - \ln \left(\frac{k_2}{k_1} \right) \right]}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$\begin{aligned}
&= \frac{(1.987 \text{ cal mol}^{-1} \text{ K}^{-1}) \left[\ln \left(\frac{294}{560} \right) - \ln (1 \times 10^{-16}) \right]}{(0.0034 - 0.0018) \text{ K}^{-1}} \\
&= 45 \text{ kcal mol}^{-1}
\end{aligned}$$

(b) To get ΔS^\ddagger , choose a point, say $(T, k) = (300 \text{ K}, 1 \times 10^{-16} \text{ s}^{-1})$, and use the expansion

$$\ln k_2 = \ln \left(\frac{kT}{h} \right) - \frac{\Delta H^\ddagger}{kT} + \frac{\Delta S^\ddagger}{k}$$

and rearrange to get

$$\begin{aligned}
\Delta S^\ddagger &= k \left[\ln \left(\frac{k_2}{\frac{kT}{h}} \right) + \frac{\Delta H^\ddagger}{kT} \right] \\
&= (1.987 \text{ cal mol}^{-1} \text{ K}^{-1}) \left[\ln \left(\frac{1 \times 10^{-16} \text{ s}^{-1}}{6.25 \times 10^{12} \text{ s}^{-1}} \right) + \frac{45,000 \text{ cal mol}^{-1}}{600 \text{ cal mol}^{-1}} \right] \\
&= 17 \text{ cal mol}^{-1} \text{ K}^{-1}
\end{aligned}$$

(c) $(1.4 \times 10^{17})(1 \times 10^{-16} \text{ s}^{-1}) = 14 \text{ s}^{-1}$

(d) The binding constant is simply the rate enhancement, 1.4×10^{17} . This is one of the largest catalytic rate enhancements known.

8. Rate increase with temperature.

A rule-of-thumb used to be that chemical reaction rates would roughly double for a ten-degree increase in temperature, say from $T_1 = 300 \text{ K}$ to $T_2 = 310 \text{ K}$. For what activation energy E_a would this be exactly correct?

Using $k_2/k_1 = 2$ gives

$$E_a = \frac{R \ln 2}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(1.987 \text{ cal mol}^{-1} \text{ K}^{-1}) \ln 2}{(3.33 \times 10^{-3} - 3.226 \times 10^{-3}) \text{ K}^{-1}} = 12.8 \text{ kcal mol}^{-1} = 53.5 \text{ kJ/mol}$$

This rule of thumb is not particularly useful in general.

9. Catalytic rate enhancement.

The reaction rate of an uncatalyzed reaction is $k_0 = 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at $T = 300 \text{ K}$. A catalyst C binds to the transition state with free energy $\Delta G = -5 \text{ kcal mol}^{-1}$. What is the rate k_c of the catalyzed reaction at $T = 300 \text{ K}$?

$$\frac{k_c}{k_0} = \overline{K} = \exp^{-\Delta G/kT} = \exp\left[\frac{5000 \text{ cal mol}^{-1}}{(2 \text{ cal mol}^{-1} \text{ K}^{-1})(300 \text{ K})}\right] = 4160$$

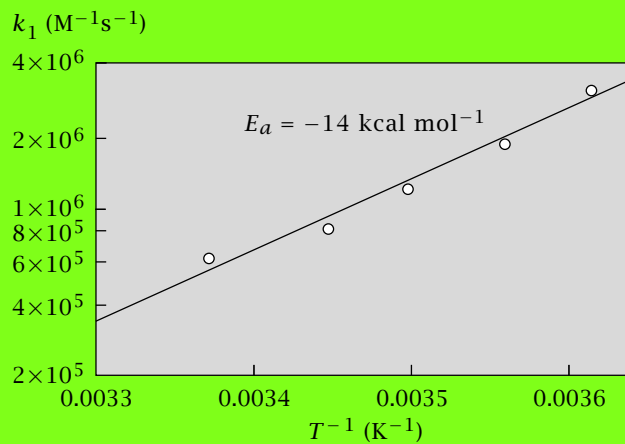
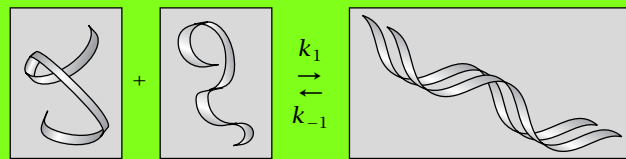
Therefore $k_c = 4160k_0 = 4.16 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$.

10. Negative activation energies.

Activation energy barriers often indicate a process that is rate-limited by the need to break a critical bond, or achieve some particular strained state. In contrast, some processes involve *negative* activation energies—their rates decrease with increasing temperature (see the figures below. Table 247 shows some Arrhenius parameters for the formation of duplex nucleic acids from single strands of various nucleotide sequences. The second figure shows an example of the kind of data from which the parameters in the table were derived. Which molecules have negative activation energies?

Relaxation kinetics of oligonucleotides (21° C to 23° C). Source: CR Cantor and PR Schimmel, Biophysical Chemistry, Volume 3, WH Freeman, San Francisco, 1980.

Ordered form	k_1 ($\text{M}^{-1}\text{s}^{-1}$)	E_a (kcal mol^{-1})
$\text{A}_9 \cdot \text{U}_9$	5.3×10^5	-8
$\text{A}_{10} \cdot \text{U}_{10}$	6.2×10^5	-14
$\text{A}_{11} \cdot \text{U}_{11}$	5.0×10^5	-12
$\text{A}_{14} \cdot \text{U}_{14}$	7.2×10^5	-17.5
$\text{A}_4\text{U}_4 \cdot \text{A}_4\text{U}_4$	1.0×10^6	-6
$\text{A}_5\text{U}_5 \cdot \text{A}_5\text{U}_5$	1.8×10^6	-4
$\text{A}_6\text{U}_6 \cdot \text{A}_6\text{U}_6$	1.5×10^6	-3
$\text{A}_7\text{U}_7 \cdot \text{A}_7\text{U}_7$	8.0×10^5	+5
$\text{A}_2\text{GCU}_2 \cdot \text{A}_2\text{GCU}_2$	1.6×10^6	+3
$\text{A}_3\text{GCU}_3 \cdot \text{A}_3\text{GCU}_3$	7.5×10^5	+7
$\text{A}_4\text{GCU}_4 \cdot \text{A}_4\text{GCU}_4$	1.3×10^5	+8



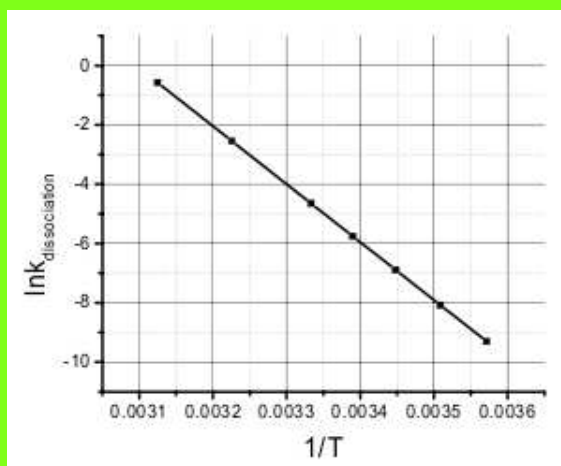
Source: CR Cantor and PR Schimmel, Biophysical Chemistry, Volume 3, WH Freeman, San Francisco, 1980.

Notice that there are 3 possible thermal signatures: positive activation energy (where rates increase with temperature), negative activation energy (where rates decrease with temperature), and entropy-dominated processes in which the rate doesn't change much with temperature. All the sequences having only A and U nucleotides appear to have negative activation energy barriers. It's not understood why. None of the cases shown are entropy-dominated.

11. Drug dissociation from DNA.

Drug *A* is an uncharged molecule containing a three-ring aromatic chromophore linked to three amino acids: valine, N-methyl valine and proline. This drug binds to double-stranded DNA, with the planar ring system intercalating between base pairs and the peptide portion lying in the minor groove.

- The aqueous solubility of Drug *A* decreases with increasing temperature. What is the sign of ΔH° for the dissolution process?
- This drug is generally poorly soluble in water, i.e. $\Delta G^\circ > 0$ for dissolution. What is the sign of ΔS° for this process?
- Give a brief explanation for your answer to part b in terms of solvent properties.
- The figure below shows data for the temperature dependence of the rate constant for dissociation of Drug *A* from duplex DNA. Use this plot to estimate the activation energy, E_a , and the entropy of activation, ΔS^\ddagger . Comment on the role of solvent in determining the value for ΔS^\ddagger .



- For the process Drug (solid) \rightarrow Drug (aqueous), the van't Hoff equation gives:

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^\circ}{RT^2}$$

And since K goes down when T goes up, ΔH° must be negative.

- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Since $\Delta H^\circ < 0$, then ΔS° must be < 0 .
- This result is unusual in that dissolution (change from solid to solution phase) usually entails an increase in S . The observed decrease in S must be due to the hydrophobic effect, that is the drug is lipophilic and thus when dissolved in water, the water undergoes an ordering which actually lowers S . This decrease in S more than compensates the increase in S due to the change in state of the drug.

(d) The Arrhenius equation for rate constant k is:

$$k = Ae^{-\frac{E_a}{RT}} \implies \ln k = \ln A - \frac{E_a}{RT}$$

Thus, $E_a = -R \cdot (\text{slope of the given plot})$

Determine the slope by picking two points on the line, such as

$$\ln k = -2 \text{ at } \frac{1}{T} = 0.0032 \text{ and } \ln k = -4 \text{ at } \frac{1}{T} = 0.0033$$

$$\implies \text{slope} = \frac{(-2 - (-4))}{0.0032 - 0.0033} = -20000$$

$$E_a = -8.314(-2000) = 166 \frac{\text{kJ}}{\text{mol}}$$

ΔS^\ddagger is related to the pre-exponential factor A by the equation:

$$A = \frac{\kappa k T}{h} e^{\frac{1 + \Delta S^\ddagger}{R}} \implies \frac{\Delta S^\ddagger}{R} = \ln\left(\frac{hA}{\kappa k T}\right) - 1$$

Set κ , the transmission factor, to 1, and determine the intercept, $\ln A$, of the plot above.

$$y = mx + b, \text{ use point } (x, y) = (0.0032, -2), m = -20000$$

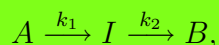
$$\implies b = y - mx = -2 + 20000 \cdot 0.0032 = 62 = \ln A$$

$$A = 8.438 \cdot 10^{26} \implies \Delta S^\ddagger = 262 \frac{\text{J}}{\text{K}}$$

This represents an increase in S, which is expected when a complex of drug with DNA starts to fall apart. Working against this increase in S is a decrease in S due to partial ordering of water around the lipophilic drug as it starts to come off the DNA, and hence be exposed to water. However, the net balance appears to be in favor the increase in S due to the loosening of the complex.

12. Series vs. parallel reactions.

- (a) You have a reaction in which A converts to B through 2 steps in series:



where the temperature dependencies of the steps are given by the Arrhenius law:

$$\begin{aligned} k_1 &= a \exp(-E_1/(RT)) \text{ and} \\ k_2 &= a \exp(-E_2/(RT)). \end{aligned}$$

Derive an expression for the total rate k_{tot} , from A to B , as a function of a , E_1 , E_2 , and T . (Hint: the time from A to B is the sum of times, A to I and I to B).

- (b) Now consider instead 2 steps in parallel:



Using the same Arrhenius equations above for the individual steps, derive the temperature dependence for k in this case. (Hint: now, the rates add.)

- (a) Since the times add,

$$\begin{aligned} t_{tot} &= t_1 + t_2 \\ \frac{1}{k_{tot}} &= \frac{1}{k_1} + \frac{1}{k_2} \\ k_{tot} &= \frac{k_1 k_2}{k_1 + k_2} \\ k_{tot} &= \frac{A e^{-\frac{E_1 + E_2}{RT}}}{e^{-\frac{E_1}{RT}} + e^{-\frac{E_2}{RT}}} \end{aligned}$$

- (b) Since the rates add,

$$k_{tot} = k_1 + k_2 = A(e^{-\frac{E_1}{RT}} + e^{-\frac{E_2}{RT}})$$

13. A cricket thermometer.

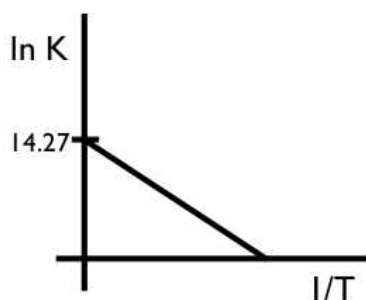
The frequency that crickets chirp increase with temperature. You can calculate the temperature in degrees Celsius by adding 4 to the number of chirps you hear from a cricket in 8 seconds. In this way, you can use a cricket as a thermometer.

- What four temperatures would you have measured if the number of chirps in 8 seconds were 16, 21, 26, and 31?
- From this data, make an Arrhenius plot and calculate the activation energy in kcal/mol. This will tell you about a rate-limiting biochemical reaction that underlies cricket chirping.
- You observe that crickets outside a fast-food restaurant chirp faster than their cousins in the wild. The fast-food crickets chirp 30 times in 8 seconds at 25° C and 40 times in 8 seconds at 35° C. By how much did the fast-food additive reduce the activation barrier for cricket chirping?
- If the equilibrium enthalpy for the chirping reaction, Δh° , is 10 kcal/mol, what is the activation energy for the reverse chirp reaction for the normal crickets?

(a) $T(^{\circ}\text{C}) = (\# \text{ chirps in 8 seconds}) + 4$

Chirps	T(°C)	T(K)
16	20	293
21	25	298
26	30	303
31	35	308

(b) Plot $\ln K$ vs. $\frac{1}{T} \rightarrow \ln K = -3971.8\left(\frac{1}{T}\right) + 14.27$, where K is measured in chirps/sec



$$\text{slope} = m = -\frac{E_a}{R} \Rightarrow E_a = -mR$$

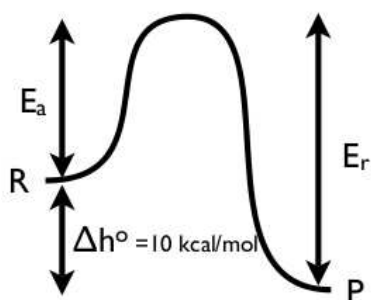
$$E_a = -(-3971.8)(8.314) = 33 \frac{\text{kJ}}{\text{mol}} = 7.89 \frac{\text{kcal}}{\text{mol}}$$

(c) Fast-food crickets: $\ln K = -2640.5(\frac{1}{T}) + 10.18$

$$E_a = -(-2640.5)(8.314) = 22 \frac{\text{kJ}}{\text{mol}} = 5.25 \frac{\text{kcal}}{\text{mol}}$$

$$\Delta E_a = 7.89 - 5.25 = 2.64 \frac{\text{kcal}}{\text{mol}}$$

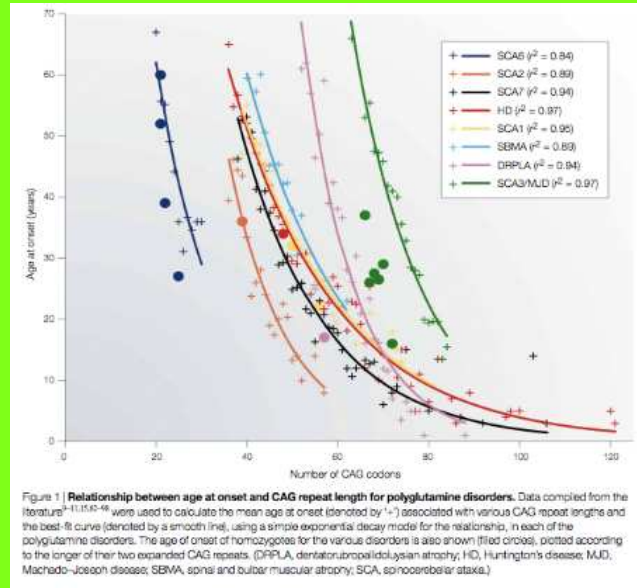
(d) Reaction Diagram:



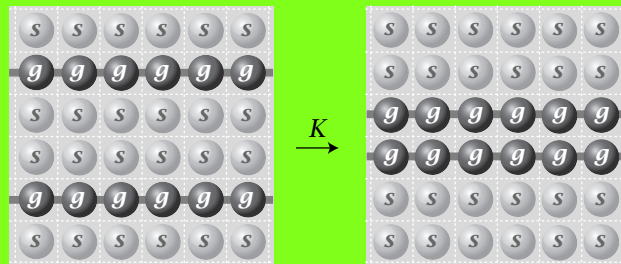
$$E_r = E_a + \Delta h^\circ = 7.89 + 10 = 17.89 \frac{\text{kcal}}{\text{mol}}$$

14. Onset of Huntington's disease.

Huntingtons is an example of a polyglutamine disease. The severity of the disease correlates with the degree of polyglutamine fibril formation. The age of onset decreases exponentially with increasing length of the polyglutamine chains (see red curve in the figure below taken from Gusella and Macdonald (2000), Nat. Review Neuroscience, 1:109-115). Fibrils form quickly after an initial nucleation event, the binding of two polyglutamine chains. Assume dimerization is the rate limiting step in the onset of the disease. Our aim is to interpret this data with a simple dimerization model.



- (a) Use the lattice model below. Define w_{ss} , w_{sg} , and w_{gg} to be the solvent-solvent, solvent-glutamine, and glutamine-glutamine interaction energies. If each glutamine chain is of length L , fill in the table below for the pairwise interactions that are broken and formed when two chains dimerize.



	w_{ss}	w_{sg}	w_{gg}
Broken			
Formed			

- (b) Write an expression for the dimerization equilibrium constant in terms of the interaction energies.
- (c) Use the expression from answering (b) to explain the exponential form of the given figure.
- (d) Estimate the polymer-solvent interaction energy, χ_{sg} , from the given figure.

(a) # Broken = # Formed

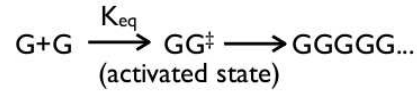
	w_{ss}	w_{sg}	w_{gg}
Broken	0	2L	0
Formed	L	0	L

(b) $K_{dim} = K_{eq} \propto e^{-\frac{\Delta\mu}{kT}}$, where $\Delta\mu = Lw_{ss} + Lw_{gg} - 2Lw_{sg}$

$$K_{dim} = \left(\frac{q_{dimer}}{q_{monomer}}\right) e^{-\frac{Lw_{ss} + Lw_{gg} - 2Lw_{sg}}{kT}}$$

$$K_{dim} = \left(\frac{q_{dimer}}{q_{monomer}}\right) e^{-\frac{L(w_{ss} + w_{gg} - 2w_{sg})}{kT}}$$

(c) Assume the rate of onset of the disease = $K_{dim}[dimer][free\ monomer]$



rate of onset $\propto 1/(\text{time of onset})$

$$\text{rate of onset of [dimer]} \propto K_{eq} \propto e^{-\frac{L(w_{ss} + w_{gg} - 2w_{sg})}{kT}} \implies \text{time of onset} \propto \frac{1}{e^{-\frac{L(w_{ss} + w_{gg} - 2w_{sg})}{kT}}}$$

$$\implies \text{time of onset} \propto e^{\frac{L(w_{ss} + w_{gg} - 2w_{sg})}{kT}}, \text{ since } z = 2.$$

$$\implies \text{time of onset} \propto e^{-L\chi_{sg}}, \chi_{sg} = \frac{z}{kT} \left(w_{sg} - \frac{w_{ss} + w_{gg}}{2} \right)$$

(d) Plot $\ln(\text{age of onset})$ vs. L , or pick two values:

$$time_1 = 60, L_1 = 40$$

$$time_2 = 5, L_2 = 100$$

$$time_2 - time_1 = e^{-(L_2 - L_1)\chi_{sg}}$$

$$\ln\left(\frac{time_2}{time_1}\right) = -(L_2 - L_1)\chi_{sg}$$

$$\ln\left(\frac{5}{60}\right) = -(100 - 40)\chi_{sg}$$

$$\implies \chi_{sg} \approx 0.04, G \text{ and } S \text{ like each other less than they like themselves.}$$

Chapter 22

Electrochemical Equilibria

1. A charged protein.

Model a protein as a sphere with a radius of 20 Å and a charge of 20e in water at 25° C and $D_{\text{water}} = 78.54$. Assume the sphere is uniformly charged on its surface.

- (a) In units of kT , what is the potential at a distance 30 Å from the protein surface?
- (b) What is the electrostatic free energy of the charge distribution on the protein in kcal mol⁻¹?

- (a) Outside of the sphere of charge, we can consider it to be a point charge at the sphere's center. Additionally, since the point is far away compared to the diameter of the sphere, we can neglect the perturbation of the dielectric by the sphere and assume a uniform dielectric of 78.54. ψ is therefore given by

$$\begin{aligned} \frac{e\psi}{kT} &= C \frac{q}{Dr} \cdot \frac{e}{kT} \\ &= \frac{(8.988 \times 10^9 \text{ kg m}^3 \text{ C}^{-2} \text{ s}^{-2})(20)(1.602 \times 10^{-19} \text{ C})^2}{(78.54)[(20 + 30) \times 10^{-10} \text{ m}](1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} \cdot \frac{\text{J}}{\text{kg m}^2 \text{ s}^{-2}} \\ &\approx 2.85 \end{aligned}$$

- (b) The free energy of charging a hollow sphere with uniform surface charge is given by Equation (22.57):

$$\Delta G_{\text{el}} = \frac{Cq^2}{2Da}$$

$$\begin{aligned}
&= \frac{8.988 \times 10^9 \text{ kg m}^3}{\text{C}^2 \text{s}^2} \cdot \frac{(20)^2 (1.602 \times 10^{-19} \text{ C})^2}{(2)(78.54)(20 \times 10^{-10} \text{ m})} \cdot \frac{\text{J}}{\text{kg m}^2 \text{s}^{-2}} \\
&\quad \cdot \frac{6.022 \times 10^{23}}{\text{mol}} \cdot \frac{1 \text{ kcal}}{4184 \text{ J}} \\
&\approx 42.3 \text{ kcal mol}^{-1}
\end{aligned}$$

2. pK_a 's in a protein.

Suppose that the protein in problem 1 has an aspartic acid residue and a lysine residue at its surface. In bulk water the pK_a of the aspartic acid side group is 3.9, and the pK_a of the lysine NH_2 side group is 10.8. What are the pK_a 's of these groups in a protein if it has a net charge of $+20e$?

Use Equation (22.37):

$$\begin{aligned}
\text{Asp : } pK_{app} &= 3.9 - \frac{0.4343 z l_B}{a} = 3.9 - \frac{0.4343(20)(7.13 \text{ \AA})}{20 \text{ \AA}} \\
&= 0.80 \\
\text{Lys : } pK_{app} &= 10.8 - \frac{0.4343(20)(7.13 \text{ \AA})}{20 \text{ \AA}} \\
&= 7.70
\end{aligned}$$

3. Acid dissociation near a protein.

Now put the protein of problems 1 and 2 in a 0.01 M aqueous solution of acetic acid (HAc). In bulk solution the acetic acid has a $pK_a = 4.0$. It is dissociated to give ion concentrations $[\text{H}^+]_{\text{bulk}}$ and $[\text{Ac}^-]_{\text{bulk}}$.

- What are the concentrations of H^+ and Ac^- ions at a location x near the protein where the potential is $\psi(x)$?
- What is the pK_a of the acetic acid near the protein at x ? Explain the difference between the situation of this acid and the situation of the aspartic acid in problem 2.

- (a) Since both ions can freely diffuse, use Equation (22.33):

$$\begin{aligned} [\text{H}^+]_{\text{x}} &= [\text{H}^+]_{\text{bulk}} e^{-\frac{e\psi(\text{x})}{kT}} \\ [\text{Ac}^-]_{\text{x}} &= [\text{Ac}^-]_{\text{bulk}} e^{+\frac{e\psi(\text{x})}{kT}} \end{aligned}$$

- (b) As with uncharged compounds, the dissociation constant K_a is determined by short-range binding interactions and by local concentrations. So we have

$$\begin{aligned} K_a(x) &= \frac{[\text{H}^+]_{\text{x}} [\text{Ac}^-]_{\text{x}}}{[\text{HAc}]_{\text{x}}} \\ &= \frac{[\text{H}^+]_{\text{bulk}} e^{-\frac{e\psi(\text{x})}{kT}} [\text{Ac}^-]_{\text{bulk}} e^{+\frac{e\psi(\text{x})}{kT}}}{[\text{HAc}]_{\text{bulk}}} \\ &\quad ([\text{HAc}] \text{ same throughout since uncharged, so unaffected by } \psi(x)) \\ &= \frac{[\text{H}^+]_{\text{bulk}} [\text{Ac}^-]_{\text{bulk}}}{[\text{HAc}]_{\text{bulk}}} \\ &= K_a(\infty) \end{aligned}$$

For the aspartic acid at the protein surface, only the H^+ has a Boltzmann distribution, because the acid ion cannot diffuse freely. In fact, the ratio $[\text{acid}^-]/[\text{acid}]$ depends on $\psi(x)$ only through $[\text{H}^+]$, not directly.

4. Acids and bases near a charged surface.

On a negatively charged surface:

- (a) Are basic groups ionized more or less than in bulk water?
- (b) Are acid groups ionized more or less than in bulk water?

- (a) More. Bases will pick up protons and become net positively charged. Near a negatively charged surface, this charge-charge interaction becomes much more favorable.
- (b) Less. Acids lose protons to become negatively charged. Near a negatively charged surface, this ionized state becomes more unfavorable.

5. Free energy of charging a sphere.

A sphere with radius a in a medium with dielectric constant D is uniformly filled with a charge of volume density ρ . Derive the electrical free energy of this sphere in two different ways:

- Derive the potential field and then charging the sphere from charge density 0 to ρ .
- Add fully charged shells of thickness dr from $r = 0$ to $r = a$.

- A shell of radius $R < a$, and thickness dR contributes to the potential inside the shell and outside the shell:

$$\text{Equation (21.45): } d\psi_{in} = \frac{\rho \cdot 4\pi R^2 dR}{4\pi\epsilon_0 D R} = \frac{\rho}{\epsilon_0 D} R dR \quad r < R$$

$$\text{Equation (21.41): } d\psi_{out} = \frac{\rho \cdot 4\pi R^2 dR}{4\pi\epsilon_0 D r} = \frac{\rho}{\epsilon_0 D} \frac{R^2}{r} dR \quad r > R$$

Total potential at $r < a$:

$$\begin{aligned} \psi &= \int_{R=0}^{R=r} d\psi_{out} + \int_{R=r}^{R=a} d\psi_{in} \\ &= \frac{\rho}{\epsilon_0 D} \left[\int_{R=0}^{R=r} \frac{R^2}{r} dR + \int_{R=r}^{R=a} R dR \right] \\ &= \frac{\rho}{\epsilon_0 D} \left(\frac{R^3}{3r} \Big|_{R=0}^r + \frac{R^2}{2} \Big|_{R=r}^a \right) \\ &= \frac{\rho}{\epsilon_0 D} \left(\frac{1}{2} a^2 - \frac{1}{6} r^2 \right) \end{aligned}$$

$$\begin{aligned} \text{So } \Delta G_{el} &= \frac{1}{2} \int \rho \psi dV \\ &= \frac{1}{2} \int_{r=0}^a \rho \cdot \frac{\rho}{\epsilon_0 D} \left(\frac{1}{2} a^2 - \frac{1}{6} r^2 \right) \cdot 4\pi r^2 dr \\ &= \frac{2\pi\rho^2}{\epsilon_0 D} \int_{r=0}^a \left(\frac{1}{2} a^2 r^2 - \frac{1}{6} r^4 \right) \\ &= \frac{4\pi}{15} \frac{\rho^2 a^5}{\epsilon_0 D} \end{aligned}$$

(b) Sphere with radius r has surface potential ψ_r as if all charge for $\leq r$ was at center:

$$\begin{aligned}\psi_r &= \rho \cdot \frac{4}{3}\pi r^3 \frac{1}{4\pi\epsilon_0 D r} \\ &= \frac{\rho r^2}{3\epsilon_0 D}\end{aligned}$$

Adding a shell with thickness dr costs

$$d(\Delta G_{el}) = \psi_r \cdot \rho \cdot 4\pi r^2 dr$$

$$\begin{aligned}\text{Total work: } \Delta G_{el} &= \int_{r=0}^{r=a} d(\Delta G_{el}) \\ &= \int_{r=0}^{r=a} \frac{\rho r^2}{3\epsilon_0 D} \cdot \rho \cdot 4\pi r^2 dr \\ &= \frac{4\pi\rho^2}{3\epsilon_0 D} \int_{r=0}^{r=a} r^4 dr \\ &= \frac{4\pi}{15} \frac{\rho^2 a^5}{\epsilon_0 D}\end{aligned}$$

6. Burying a charge in a protein.

As an estimate for the free energy of burying a charged amino acid such as aspartic or glutamic acid in protein folding, compute the free energy of transferring an ion of radius 3 Å and charge +1 from water to oil. Assume that water has a dielectric constant $D_w = 80$, and oil has $D_o = 2$.

Use the Born energy expression,

$$\Delta G = \frac{Cq^2}{2a} \left(\frac{1}{D_2} - \frac{1}{D_1} \right)$$

in terms of the Bjerrum length in vacuum

$$\frac{\Delta G}{kT} = \frac{l_B}{2a} \left(\frac{1}{D_2} - \frac{1}{D_1} \right)$$

$$= \frac{560 \text{ \AA}}{(2)(3 \text{ \AA})} \left(\frac{1}{2} - \frac{1}{80} \right)$$

$$\approx 45.5$$

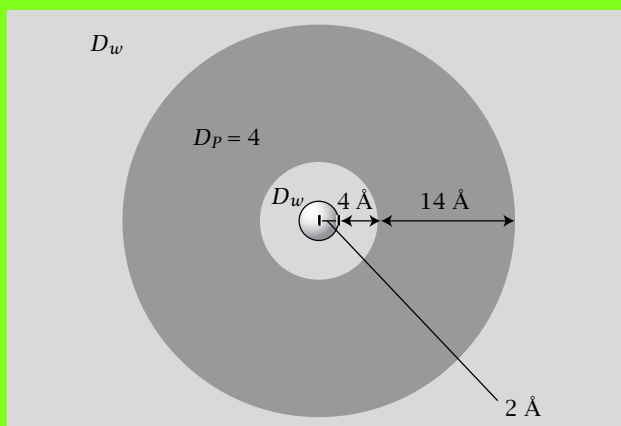
For $T = 300 \text{ K}$,

$$\Delta G = 45.5 \cdot \frac{1.987 \text{ cal}}{\text{K mol}} \cdot 300 \text{ K} \approx 27.1 \text{ kcal mol}^{-1}$$

7. A solvated charge in a protein.

The Born energy in Equation (22.55) allows you to estimate the free energy cost for a charged group to be deep inside a fully folded protein (instead of at the protein surface in contact with water). Estimate the free energy cost for a charged group to stay inside a *partly* folded protein. Consider the ionic group as a sphere with radius 2 \AA and total surface charge e (see the figure below). This group is first surrounded by a shell of bulk water, 4 \AA thick. This in turn is surrounded by a shell of protein, 14 \AA thick with dielectric constant $D_P = 4$, which is in contact with bulk water at 25° C . Derive the electrostatic free energy of the ionic group

- (a) in water,
- (b) in the partly folded protein, and
- (c) as in (b) but with the water shell replaced by protein, $D_P = 4$, to simulate the completely folded protein.



(a) Use Equation (22.57):

$$\Delta G_w = \frac{\mathcal{C}q^2}{2D_w a} = \frac{(7.13 \text{ \AA})}{(2)(2 \text{ \AA})} \cdot kT = 1.78kT = 1.06 \text{ kcal mol}^{-1}$$

(b) To get the charge inside the protein, we (1) discharge the sphere of part (a), (2) transfer into the hydrophobic region, (3) transfer from the hydrophobic region into the water cavity, and (4) recharge the sphere. So

$$\Delta G_{pf} = \frac{\mathcal{C}q^2}{2D_w a} - \frac{\mathcal{C}q^2}{2D_w a} + 0 + 0 + \frac{\mathcal{C}q^2}{2D_w a} = \Delta G_w,$$

the same as part (a)

(c) Use Equation (22.57) again, with $D = 4$:

$$\Delta G_f = \frac{\mathcal{C}q^2}{2D_p a} = \frac{(7.13 \text{ \AA})}{(2)(2 \text{ \AA})} \cdot \frac{78.54}{4} \cdot kT = 35kT = 20.7 \text{ kcal mol}^{-1}$$

This is a much more unfavorable situation.

8. Oil/water interfacial potential.

Consider an uncharged oil/water interface. On the aqueous side, the proximity of the oil phase biases the orientation of the water molecules in an unknown way. Calculate the resulting potential across the boundary layer for the maximum bias, the complete line-up of the first layer of water dipoles perpendicular to the interface. Treat this layer as a parallel plate capacitor, with one water molecule occupying 10 \AA^2 of the interfacial area. The dipole moment is $\mu = 1.85$ Debye (1 Debye = $3.336 \times 10^{-30} \text{ C m}$) per water molecule. Take two values of the dielectric constant D between the capacitor plates:

(a) $D = 2$, as for oil, and

(b) $D = 80$, as for bulk water.

(If water is perfectly oriented, a situation called dielectric saturation, $D = 2$ is more likely.)

Let water be a dipole of charges $+q$ and $-q$ separated by distance d . Then the charge density of the “plate” surface is $\sigma = q/10 \text{ \AA}^2$. So we can calculate the potential across this boundary

“capacitor” as

$$\Delta\psi = \frac{\sigma d}{\varepsilon_0 D} = \frac{\left(\frac{q}{4\pi\epsilon_0^2}\right)d}{\varepsilon_0 D} = \frac{\mu}{(10\text{ \AA}^2)\varepsilon_0 D}$$

(a) For D=2

$$\begin{aligned}\Delta\psi &= \frac{(1.85\text{ D})\left(3.336 \times 10^{-30} \frac{\text{C m}}{\text{D}}\right)}{(10 \times 10^{-20} \text{ m}^2)\left(8.85 \times 10^{-12} \frac{\text{C}^2}{\text{J m}}\right)} (2) \\ &= 3.48\text{ V}\end{aligned}$$

(b) For D=80

$$\begin{aligned}\Delta\psi &= \frac{(1.85\text{ D})\left(3.336 \times 10^{-30} \frac{\text{C m}}{\text{D}}\right)}{(10 \times 10^{-20} \text{ m}^2)\left(8.85 \times 10^{-12} \frac{\text{C}^2}{\text{J m}}\right)} (80) \\ &= 87.2\text{ mV}\end{aligned}$$

Even an uncharged oil/water interface can have a significant interfacial potential.

9. Small electrostatic potentials.

For a monovalent ion at $T = 300\text{ K}$, what is the value of ψ such that $e\psi = kT$?

$$\begin{aligned}\psi &= \frac{kT}{e} = \frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(300\text{ K})}{1.602 \times 10^{-19} \text{ C}} \\ &= 25.8\text{ mV}\end{aligned}$$

10. Sodium potential in a frog muscle.

Inside a frog muscle cell, the sodium concentration is $[\text{Na}]_{\text{in}} = 9.2 \text{ mM}$. Outside, the sodium concentration is $[\text{Na}]_{\text{out}} = 120 \text{ mM}$.

- (a) Compute the sodium potential $\Delta\psi$ across the membrane, at $T = 300 \text{ K}$.
- (b) Which side of the membrane has the more positive potential, the inside or the outside?

- (a) Use Equation (22.25):

$$\begin{aligned}\Delta\psi &= \psi_{\text{in}} - \psi_{\text{out}} = \frac{kT}{e} \ln \frac{[\text{Na}^+]_{\text{out}}}{[\text{Na}^+]_{\text{in}}} \\ &= (25.8 \text{ mV}) \ln \frac{120 \text{ mM}}{9.2 \text{ mM}} = 66 \text{ mV}\end{aligned}$$

- (b) The inside, since $\Delta\psi > 0 \implies \psi_{\text{in}}$ is more positive.

11. Membrane pores.

A neutral protein ‘carrier’ may help an ion to transfer into and across a lipid membrane.

- (a) What is the electrostatic free energy change when a monovalent ion is transferred from water at 25° C to a hydrocarbon solvent with dielectric constant $D_{\text{hc}} = 2$? The radius of the ion is 2 \AA .
- (b) Now wrap the ion in a neutral protein to produce a spherical complex with radius $b = 15 \text{ \AA}$. What is the electrostatic free energy of transfer from water to hydrocarbon of the ion–protein complex?

For both parts, use Equation (22.63)

$$\begin{aligned}\text{(a)} \quad \Delta G_{el} &= \frac{e^2}{2r} \left(\frac{1}{D(\text{hc})} - \frac{1}{D(\text{water})} \right) = \frac{l_B}{2r} \left(\frac{1}{D(\text{hc})} - \frac{1}{D(\text{water})} \right) \cdot kT \\ &= \frac{560 \text{ \AA}}{2(2 \text{ \AA})} \left(\frac{1}{2} - \frac{1}{78.54} \right) (1.987 \text{ kcal mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})\end{aligned}$$

$$= 40.4 \text{ kcal mol}^{-1}$$

highly unfavorable.

$$\begin{aligned} \text{(b)} \quad \Delta G_{el} &= \frac{560 \text{ \AA}}{2(15 \text{ \AA})} \left(\frac{1}{2} - \frac{1}{78.54} \right) (1.987 \text{ kcal mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \\ &= 5.39 \text{ kcal mol}^{-1} \end{aligned}$$

much less unfavorable.

12. Solvating a protein.

A spherical protein has a valency of $z = -5$, and a radius of $a = 10 \text{ \AA}$. The change in electrostatic free energy, ΔG_{el} , when you transfer the protein from vacuum ($D = 1$) to water ($D \approx 80$) is a part of the solvation free energy. Compute ΔG_{el} .

We use here radius $a = 10 \text{ \AA}$. Equation (22.65) gives us

$$\begin{aligned} \Delta G_{el} &= \frac{Cq^2}{2a} \left(\frac{1}{D_2} - \frac{1}{D_1} \right) = \frac{25 l_B}{2a} \left(\frac{1}{D_2} - \frac{1}{D_1} \right) \cdot kT \\ &= \frac{25(560 \text{ \AA})}{2(10 \text{ \AA})} \left(\frac{1}{80} - 1 \right) (1.987 \text{ kcal mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \\ &= -409.5 \text{ kcal mol}^{-1} \end{aligned}$$

Solvation is extremely favorable.

13. Burying an ion pair in oil.

What is the free energy cost of transferring a monovalent anion of radius $a = 2 \text{ \AA}$ and a monovalent cation of the same radius a from vacuum into oil ($D = 2$) at an ion-paired separation of $2a$?

Calculate this transfer by breaking into 3 steps: (1) separate the two ions to infinite distance, (2) transfer each from vacuum into oil, (3) bring the two ions back together. Combine the

energy changes for each step, to get:

$$\begin{aligned}\Delta G_{el} &= \frac{\mathcal{C}e^2}{2a(1)} + 2 \cdot \frac{\mathcal{C}e^2}{2a} \left(\frac{1}{2} - 1 \right) - \frac{\mathcal{C}e^2}{2a(2)} \\ &= \frac{\mathcal{C}e^2}{2a(1)} \left(1 - 1 - \frac{1}{2} \right) = -\frac{\mathcal{C}e^2}{4a} \\ &= -\frac{(560 \text{ \AA})(1.987 \text{ kcal mol}^{-1})(298.15 \text{ K})}{4(2 \text{ \AA})} \\ &= -41.5 \text{ kcal mol}^{-1}\end{aligned}$$

The transfer from vacuum is favorable.

14. Temperature dependent dielectric constants.

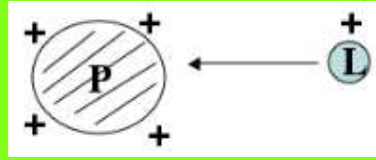
Show that Coulombic interactions between charges in liquids can have an entropic component if the dielectric constant, D , depends on temperature.

Equation 20.66 of MDF shows how to get the enthalpic component for dielectric constants that change with temperature; there's also an entropic part.

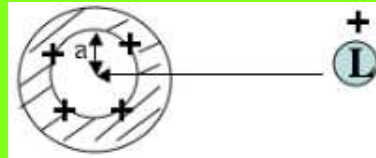
15. Ligand-protein electrostatic interactions.

Consider a ligand with charge of $+1e$ and a spherical protein of $+4e$ and radius of 20 \AA in water ($D = 80$).

- (a) What is the work of bringing the ligand from $r = \infty$ to the surface of the protein?



- (b) Now assume there is a hollow cavity of radius $a = 5 \text{ \AA}$ inside the protein. The protein cavity is filled with water, and there is a net charge of $+4e$ on the shell surrounding the cavity. What is the work of transferring the ligand from the bulk water solution far away from the protein to the center of the water filled cavity?



- (c) Now consider the ligand to be an uncharged carboxylic acid with $pK_a = 3.0$. If you bring this ligand into the water-filled protein cavity as described in part (b), what will be its apparent pK_a ?

- (a) Work to bring ligand from $r = \infty$ to $r = 20 \text{ \AA}$

$$\text{Work} = \psi_a, \psi_r = \frac{eQ}{Dr} = \frac{1}{4\pi\epsilon_0} \frac{4e}{80(20 \cdot 10^{-10} \text{ m})}$$

$$\psi_r = \frac{4(1.6 \cdot 10^{-19} \text{ C})}{4\pi(8.89 \cdot 10^{-19} \frac{\text{C}}{\text{V} \cdot \text{m}})(80)(20 \cdot 10^{-10} \text{ m})}$$

$$\psi_r = 0.3596 \text{ V}$$

$$\text{Work} = \psi_q = 0.03596(e) = 5.755 \cdot 10^{-21} \text{ J}$$

- (b) Potential inside charged spherical shell:

$$\psi_{in} = \frac{Cq}{Da}, \text{ where } a = \frac{1}{4}r$$

$$\text{So } \psi_{in} = 4\psi_r, W = \psi_r q = 2.3 \cdot 10^{-20} \text{ J}$$

- (c) $pK_{app}(r_L = 0) = pK_a(\infty) - \frac{0.4343e\psi(r < a)}{kT}$

$$pK_{app}(r_L = 0) = 3 - \frac{0.4343(1.6 \cdot 10^{-19} \text{ C})(4 \cdot 0.03596 \text{ V})}{(1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}})(298 \text{ K})}$$

$$pK_{app}(r_L = 0) = 3 - 2.43 = 0.57$$

The RCOOH group is more acidic inside a cavity with a positively charged shell.

Chapter 23

Salt Ions Shield Charged Objects

1. The potential around colloidal spheres.

What is the dimensionless surface potential $\Phi = e\psi/kT$ at a distance of 50 Å from

- (a) A colloidal sphere with a radius of 20 Å and charge 20e in pure water?
- (b) The same sphere in 0.1 M NaCl at 25° C?
- (c) What are the potentials in volts?

$$\begin{aligned}
 \text{(a)} \quad \phi &= \frac{e\psi}{kT} = \frac{\mathcal{C}qe}{DrkT} \\
 &= \frac{q l_B}{e r} = 20 \cdot \frac{7.13 \text{ Å}}{50 \text{ Å}} \\
 &= 2.85
 \end{aligned}$$

(b) Use Equation (23.22), with $1/\kappa = 9.62 \text{ Å}$

$$\begin{aligned}
 \phi &= \frac{e\psi}{kT} = \frac{\mathcal{C}qe}{DrkT(1 + \kappa a)} e^{-\kappa(r-a)} \\
 &= \frac{20(7.13 \text{ Å})}{(50 \text{ Å})(1 + \frac{20 \text{ Å}}{9.62 \text{ Å}})} e^{-\frac{50 \text{ Å} - 20 \text{ Å}}{9.62 \text{ Å}}}
 \end{aligned}$$

$$= 0.041$$

$$(c) \quad \frac{kT}{e} = \frac{(1.38 \times 10^{-23} \text{ J K}^{-1})(298.15 \text{ K})}{(1.602 \times 10^{-19} \text{ C})} = 25.7 \text{ mV}$$

$$(a) \quad \psi = \phi \cdot \frac{kT}{e} = 2.85 \cdot 25.7 \text{ mV} = 73.2 \text{ mV}$$

$$(b) \quad \psi = 0.041 \cdot 25.7 \text{ mV} = 1.05 \text{ mV}$$

2. The potential near a protein in salt solution.

Consider a protein sphere with a radius of 18 Å, and charge $Q = -10e$, in an aqueous solution of 0.05 M NaCl at 25°C. Consider the small ions as point charges and use the Debye–Hückel linear approximation of the Poisson–Boltzmann equation.

- (a) What is the dimensionless surface potential $e\psi_a/kT$ of the protein?
- (b) What are the concentrations of Na^+ and Cl^- ions at the surface of the protein?
- (c) What are the concentrations of Na^+ and Cl^- ions at a distance of 3 Å from the protein surface?

From Table 23.1, $1/\kappa = 13.6 \text{ Å}$ in 0.05 M salt solution.

$$\begin{aligned} (a) \quad \frac{e\psi_a}{kT} &= \frac{\mathcal{C}qe}{DkTa(1 + \kappa a)} \\ &= \frac{(-10)(7.13 \text{ Å})}{(18 \text{ Å})(1 + \frac{18 \text{ Å}}{13.6 \text{ Å}})} \\ &= -1.705 \end{aligned}$$

- (b) Use Equations (23.1) and (23.2) to get the concentrations at the protein face:

$$[\text{Na}^+] = 0.05e^{1.705} = 275 \text{ mM}$$

$$[\text{Cl}^-] = 0.05e^{-1.705} = 9.1 \text{ mM}$$

(c) Following Equation (23.18), the potential at $r = 21\text{\AA}$ is

$$\frac{e\psi}{kT} = \frac{e\psi_a}{kT} \frac{a}{r} e^{-\kappa(r-a)} = -1.705 \cdot \frac{18\text{\AA}}{21\text{\AA}} e^{-\frac{3\text{\AA}}{13.6\text{\AA}}} = -1.172$$

Therefore

$$\begin{aligned} [\text{Na}^+] &= 0.05e^{1.172} = 161\text{ mM} \\ [\text{Cl}^-] &= 0.05e^{-1.172} = 15.5\text{ mM} \end{aligned}$$

3. Surface potentials and Debye lengths.

You have a uniformly charged sphere with radius $a = 50\text{\AA}$ in a 0.02 M NaCl solution. At a distance of 30\AA from the surface of the sphere the potential $\psi = 20\text{ mV}$.

- What is the Debye length $1/\kappa$ in the solution?
- What is the surface potential ψ_a of the sphere? (Assume that the potential field in the solution around the sphere can be derived from the linear Poisson–Boltzmann equation.)
- What is the charge Q on the sphere?
- Sketch the potential as a function of distance from the sphere.

(a) Table 23.1 tells us that $1/\kappa = 21.5\text{\AA}$ for a 0.02 M solution

(b) Rearrange Equation (23.18) to get

$$\begin{aligned} \psi_a &= \psi(r) \frac{r}{a} e^{\kappa(r-a)} = 20\text{ mV} \cdot \frac{80\text{\AA}}{50\text{\AA}} \cdot e^{\frac{30\text{\AA}}{21.5\text{\AA}}} \\ &= 129.16\text{ mV} \end{aligned}$$

(c) The number of elementary charges e on the sphere follow from Equation (23.20):

$$\frac{Q}{e} = \frac{\psi_a}{e} 4\pi\epsilon_0 D a (1 + \kappa a)$$

It is convenient to work with the dimensionless potential:

$$\frac{e\psi_a}{kT} = \frac{\psi_a}{25.8 \text{ mV}} = \frac{129.16 \text{ mV}}{25.8 \text{ mV}} = 5.0$$

$$\begin{aligned} \text{Then } \frac{Q}{e} &= \frac{e\psi_a}{kT} \cdot \frac{4\pi\epsilon_0 DkT}{e^2} a(1 + \kappa a) = \frac{e\psi_a}{kT} \cdot l_B^{-1} \cdot a(1 + \kappa a) \\ &= 5 \cdot 7.13 \text{ \AA} \cdot 50 \text{ \AA} \left(1 + \frac{50 \text{ \AA}}{21.5 \text{ \AA}}\right) = 116.6 \end{aligned}$$

4. The potential near a plane.

You have a uniformly charged flat plate in contact with a 0.02 M NaCl solution at 25° C. At a distance of 3 nm from the plate, the potential is 30 mV.

- What is the Debye length $1/\kappa$ in the solution?
- What is the surface potential of the charged plane in mV, and in units of kT/e ? Use the linear Poisson–Boltzmann equation.
- If you had used the nonlinear Poisson–Boltzmann equation, would you find the surface potential to be larger or smaller than you found under (b)? Why?
- Use the surface potential from (b) to find the surface charge density σ of the plane.

(a) From Table 23.1, we get $1/\kappa = 21.5 \text{ \AA}$ in a 0.02 M salt solution

(b) Rearrange Equation (23.10) to get

$$\begin{aligned} \psi_0 &= \psi(x)e^{\kappa x} = (30 \text{ mV})e^{\frac{30 \text{ \AA}}{21.5 \text{ \AA}}} \\ &= 121.1 \text{ mV} \\ \phi_0 &= \frac{e\psi_0}{kT} = \frac{121.1 \text{ mV}}{25.7 \text{ mV}} \\ &= 4.71 \end{aligned}$$

(c) Larger, because the curvature of the (non-linearized) potential-distance curve is greater, while the curves for the two P-B equations coincide at large distances (both have $\psi \rightarrow 0$).

(d) From Equation (23.13)

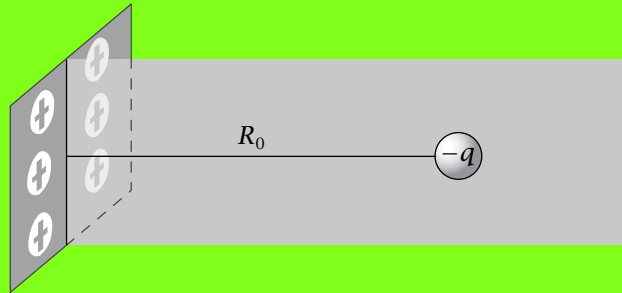
$$\begin{aligned}\frac{\sigma}{e} &= \frac{D\varepsilon_0\kappa\psi_0}{e} = \frac{kTD\varepsilon_0\phi_0\kappa}{e^2} \\ &= \frac{\kappa\phi_0}{4\pi l_B} = \frac{4.69}{(21.5 \text{ \AA})(4\pi)(7.13 \text{ \AA})} \\ &= 0.00245 \text{ \AA}^{-2}\end{aligned}$$

$$\begin{aligned}\text{or } \sigma &= (0.00245 \text{ \AA}^{-2})e = (0.00245 \times 10^{20} \text{ m}^{-2})(1.602 \times 10^{-19} \text{ C}) \\ &= 0.039 \text{ C m}^{-2}.\end{aligned}$$

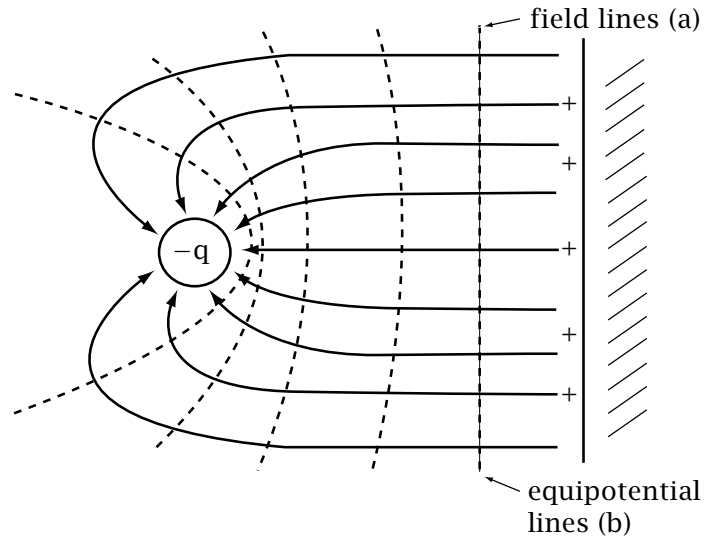
5. A charged protein near a chromatographic surface.

Consider a spherical protein in water with charge $-q$ ($q > 0$) at a distance R_0 from a planar ion chromatography column surface with net positive charge, shown in the figure below.

- Draw the field lines approximately. Include arrows to indicate the field direction.
- Draw the equipotential contours.
- If the solvent water were replaced by a water/methanol mixture with a lower dielectric constant, would it weaken or strengthen the attraction between the protein and the planar surface?



(a)



(b) Equipotential lines are \perp to field lines.

(c) It would strengthen the attraction.

6. The potential of a membrane.

Consider a phospholipid bilayer membrane consisting of 90% uncharged lipid (zwitterionic phosphatidylcholine) and 10% acid lipid (singly charged phosphatidylserine or phosphatidylglycerol). Assume 68 \AA^2 surface area per lipid head group. The membrane is in contact with an aqueous solution of NaCl concentration c_{NaCl} at 25°C . Calculate the surface potential of the membrane for $c_{\text{NaCl}} = 0.05$ and 0.1 mol^{-1} .

Inside the membrane there is no space charge: $(d^2\psi)/(dx^2) = 0$. This gives $\psi = C_1x + C_2$. At $x = -\infty$ ψ must be finite, so we choose $C_1 = 0$; therefore $\psi = C_2$. On the aqueous side we solve the linear PB equation (Equation (23.13)) which yields

$$\psi_0 = \frac{\sigma}{\kappa\epsilon_0 D}.$$

Converting to dimensionless quantities,

$$\frac{e\psi_0}{kT} = \frac{\sigma}{e} \frac{4\pi l_B}{\kappa}$$

where the Bjerrum length is $l_B = 7.13 \text{ \AA}$ and $\sigma/e = 0.1/68 \text{ \AA}^2$. In 0.05 M NaCl, $1/\kappa = 13.6 \text{ \AA}$; therefore

$$\frac{e\psi_0}{kT} = \frac{0.1}{68 \text{ \AA}^2} 4\pi (7.13 \text{ \AA})(13.6 \text{ \AA}) = 1.79$$

In 0.1 M NaCl, $1/\kappa = 9.62 \text{ \AA}$, so $e\psi_0/kT = 1.27$.

7. Binding to a membrane.

What is the electrostatic free energy of binding to the membrane in problem 6 of a trivalent positive ion such as spermidine (a biologically active polyamine), assuming that

- (a) binding occurs at the membrane surface, and
- (b) owing to steric factors, the charges of the bound spermidine stay in the water 5 \AA distant from the membrane surface?

In 0.05 M NaCl the electrostatic free energy of binding is in case (a)

$$\begin{aligned} \Delta G_b &= 3e\psi_0 = 3(1.79 kT) = 5.37 kT \quad \text{per bound molecule, or} \\ \Delta G_b &= 5.37 RT \quad \text{per mole} = 3.18 \text{ kcal/mol} \end{aligned}$$

In case (b)

$$\begin{aligned} \psi &= \psi_0 e^{-\kappa x} = \left(1.79 \frac{kT}{e} \right) e^{-\frac{5}{13.6}} = 1.24 \frac{kT}{e} \\ \text{so } \Delta G_b &= 3e\psi = 3\left(1.24 \frac{kT}{e} \right) = 3.72 kT \quad \text{per bound molecule} \\ &= 3.72 RT \quad \text{per mole} = 2.20 \text{ kcal/mol.} \end{aligned}$$

For 0.1 M NaCl, use the answers from problem 6 and the Debye length $1/\kappa = 9.62 \text{ \AA}$ to get

(a) $\Delta G_b = 2.26 \text{ kcal/mol}$ and (b) $\Delta G_b = 1.34 \text{ kcal/mol}$.

8. Electrostatic potential near a protein.

A protein in aqueous solution with 0.1 M monovalent salt has 9 positive and 22 negative charges at 25° C. It is modelled as a sphere with radius 20 Å and uniform surface charge. What is the potential in units of kT/e

(a) at the surface of the protein, and

(b) at a distance 10 Å from the protein surface into the solution?

Use (i) Coulomb's equation (no shielding by small ions) and (ii) the linear Poisson–Boltzmann equation.

(a) (i) Use Equation (21.45)

$$\frac{e\psi_a}{kT} = \frac{ze}{4\pi\epsilon_0 Da} \frac{e}{kT} = \frac{l_B z}{a} = \frac{(7.13 \text{ Å})(-13)}{20 \text{ Å}} = -4.63$$

(ii) Equation (23.20) for ψ_a is the same as case (ai) but for the extra factor $1 + \kappa a = 1 + (20/9.62) = 3.079$:

$$\frac{e\psi_a}{kT} = \frac{-4.63}{3.079} = -1.51$$

(b) (i) Use Equation (21.35)

$$\frac{e\psi}{kT} = \frac{e\psi_a}{kT} \frac{a}{a + 10 \text{ Å}} = -4.63 \frac{20 \text{ Å}}{30 \text{ Å}} = -3.09$$

(ii) We use the surface potential of (bi) with Equation (23.17)

$$\frac{e\psi}{kT} = \frac{e\psi_a}{kT} \frac{a}{a + 10 \text{ Å}} e^{-\kappa(r-a)} = -3.09 e^{-\frac{10 \text{ Å}}{9.62 \text{ Å}}} = -0.356$$

9. Debye–Hückel model.

Apply the Debye–Hückel theory to a 0.01 M monovalent salt solution at 25° C. Treat the ions as hard spheres with a radius of 2 Å. Assume $D = 80$. What is the change in chemical potential in cal mol^{-1} due to the ion interactions? What is the activity coefficient of the ions?

Apply Equation (23.29):

$$\begin{aligned}
 \Delta\psi = 2kT \ln \gamma &= -\frac{e^2}{4\pi\epsilon_0 D} \frac{\kappa}{1 + \kappa b} \\
 &= -\frac{(1.90 \times 10^{-19} \text{ C})^2}{4\pi \left(8.85 \times 10^{-12} \frac{\text{C}^2}{\text{J m}}\right) (80)} \frac{(30.4 \times 10^{-10} \text{ m})^{-1}}{1 + \frac{2(2 \text{ \AA})}{30.4 \text{ \AA}}} \\
 &= -1.18 \times 10^{-21} \frac{\text{J}}{\text{molecule}} \\
 &= (-1.18 \times 10^{-21} \text{ J})(6.022 \times 10^{23} \text{ mol}^{-1}) \left(\frac{1 \text{ cal}}{4.184 \text{ J}}\right) = -169.8 \frac{\text{cal}}{\text{mol}} \\
 \ln \gamma &= \frac{\Delta\psi}{2kT} = \frac{-1.18 \times 10^{-21} \text{ J}}{2(1.38 \times 10^{-23} \frac{\text{J}}{\text{K}})(298.15 \text{ K})} = -0.1434 \\
 \Rightarrow \gamma &= 0.866
 \end{aligned}$$

10. Electrostatic potential around a line charge.

A line charge with density λ and with length ℓ is in a salt solution with Debye length $1/\kappa$. Use Equation (23.24) to find an integral expression for the potential in the plane bisecting the line charge.

(Similar to problem 20.4(a)) Choose the z coordinate along the line charge, from $-\frac{\ell}{2}$ to $+\frac{\ell}{2}$. A piece dz at point z has charge λdz , at distance $\sqrt{r^2 + z^2}$ from P . The contribution of this charge to the potential $\psi(r)$ at P is

$$d\psi(r) = \frac{\lambda dz e^{-\kappa\sqrt{r^2+z^2}}}{4\pi\epsilon_0 D \sqrt{r^2+z^2}}$$

The total potential at P is then

$$\psi(r) = \int_{z=-\frac{\ell}{2}}^{z=+\frac{\ell}{2}} d\psi(r) = \frac{\lambda}{4\pi\epsilon_0 D} \int_{-\frac{\ell}{2}}^{\frac{\ell}{2}} \frac{e^{-\kappa\sqrt{r^2+z^2}}}{\sqrt{r^2+z^2}} dz$$

Let $y = \sqrt{\kappa^2(z^2 + r^2)}$, then

$$= \frac{\lambda}{4\pi\epsilon_0 D} \int_{-\kappa\sqrt{r^2+\frac{l^2}{4}}}^{\kappa\sqrt{r^2+\frac{l^2}{4}}} \frac{e^{-y}}{y} dy$$

The restriction is that the answer is valid only for low potential, like Equation (23.21)

11. Electrostatic potential near a vesicle.

A simple model for a spherical vesicle is a spherical shell with radius a , charge density σ , permeated by a salt solution with Debye length $1/\kappa$. Use Equation (23.24) to derive the potential outside the shell at distance r from the center.

- (a) Derive and discuss the limit of $\psi(r)$ for $\kappa \rightarrow 0$.
- (b) For the situation in (a), derive the potential inside the spherical shell. What is the limit for $\kappa \rightarrow 0$?
- (c) From the results of (a) and (b), derive the expression for the limit $\kappa a \rightarrow \infty$ and compare these with the result of Example 23.3.

- (a) Use the same set-up as with problem 7 in Chapter 21, with total charge on the sphere $q = 4\pi\sigma a^2$, and introducing the Debye term, so:

$$d\psi(r) = \frac{(4\pi\sigma a^2)}{8\pi\epsilon_0 a D r} (e^{-\kappa R}) dR = \frac{\sigma a}{2\epsilon_0 D r} (e^{-\kappa R}) dR$$

$$\begin{aligned} \text{Integrate: } \psi(r) &= \frac{\sigma a}{2\epsilon_0 D r} \int_{R=r-a}^{r+a} e^{-\kappa R} dR \\ &= \frac{\sigma a}{2\epsilon_0 D \kappa r} (e^{-\kappa(r-a)} - e^{-\kappa(r+a)}). \end{aligned}$$

For $\kappa \rightarrow 0$, remembering that $e^{-x} \approx 1 - x$ for small x :

$$\begin{aligned} \psi(r) &\approx \frac{\sigma a}{2\epsilon_0 D \kappa r} [(1 - \kappa(r-a)) - (1 - \kappa(r+a))] \\ &= \frac{\sigma a^2}{2\epsilon_0 D r} = \frac{q}{4\pi\epsilon_0 D r} \end{aligned}$$

as expected from Coulomb's Law.

- (b) Use the setup for finding the inner potential equation derived for problem 21.7, with the same changes used in part (a):

$$\begin{aligned}\psi(r) &= \frac{\sigma a}{2\varepsilon_0 D r} \int_{R=a-r}^{a+r} e^{-\kappa R} dR \\ &= \frac{\sigma a}{2\varepsilon_0 D \kappa r} \left(e^{-\kappa(a-r)} - e^{-\kappa(a+r)} \right)\end{aligned}$$

So for $\kappa \rightarrow 0$ we have $e^{-\kappa(a-r)} - e^{-\kappa(a+r)} \approx 2\kappa r$ so $\psi(r) \rightarrow \frac{\sigma a}{\varepsilon_0 D} = \frac{q}{4\pi\varepsilon_0 D a}$ as found with Coulomb's law.

- (c) With $\kappa a \rightarrow \infty$ we have $e^{-\kappa(a+r)} \rightarrow 0$, $\frac{a}{r} \rightarrow 1$ and $r - a = \delta$. So outside the charged shell we have

$$\begin{aligned}\psi_\delta &= \frac{\sigma a}{2\varepsilon_0 D \kappa r} \left(e^{-\kappa(r-a)} - e^{-\kappa(r+a)} \right) \\ &= \frac{\sigma}{2\varepsilon_0 D \kappa} e^{-\kappa\delta} \quad \delta > 0\end{aligned}$$

Inside the shell:

$$\begin{aligned}\psi_\delta &= \frac{\sigma a}{2\varepsilon_0 D \kappa r} \left(e^{-\kappa(a-r)} - e^{-\kappa(a+r)} \right) \\ &= \frac{\sigma}{2\varepsilon_0 D \kappa} e^{+\kappa\delta} \quad \delta < 0\end{aligned}$$

We have for $\kappa a \rightarrow \infty$ two flat double layers, one inside and one outside the shell, as in example 23.4.

12. Debye lengths.

In the Debye–Hückel theory of monovalent salt solutions there is a characteristic length quantity κ , defined by $\kappa^2 = (2e^2 n_\infty)/(\varepsilon_0 D k T)$, where n_∞ is the salt concentration.

- (a) Express κ in terms of the Bjerrum length ℓ_B .
- (b) For water at room temperature, $\ell_B = 7.13 \text{ \AA}$. Compute the Debye length $1/\kappa$ in \AA for a solution of $n_\infty = 1 \text{ mol L}^{-1}$.

$$(a) \quad \kappa^2 = (2)(4\pi)(n_0) \cdot \frac{e^2}{4\pi\varepsilon_0 D k T} = 8\pi n_0 \ell_B$$

$$(b) \quad \begin{aligned} \kappa^2 &= 8\pi(1 \text{ mol L}^{-1})(7.13 \times 10^{-10} \text{ m}) \\ \Rightarrow \quad \frac{1}{\kappa} &= 3.04 \text{ \AA} \end{aligned}$$

13. Ion binding to a sphere.

Compute the free energy of bringing a divalent ion into contact with a spherical particle of radius $a = 14 \text{ \AA}$, from far away. The ion has valence $z = +2$ and the particle has a valence of $Z = +20$. For water at room temperature, compute the free energy

- (a) in a solution having monovalent salt concentration 0.1 M ;
- (b) for a solution having monovalent salt concentration 0.01 M .

- (a) Use the Debye–Hückel model to get $\psi(a)$, the electrostatic potential at the surface of the charged sphere ($r = a$), with $\Delta G = q\psi(a)$:

$$\Delta G = q\psi(a) = \frac{\mathcal{C}Qq}{D_w a(1 + \kappa a)}$$

$$\text{To simplify, } kT = \frac{\mathcal{C}e^2}{D_w \ell_{Bw}}$$

$$\text{so } \frac{\Delta G}{kT} = \frac{Zz}{(1 + \kappa a)} \left(\frac{\ell_{Bw}}{a} \right)$$

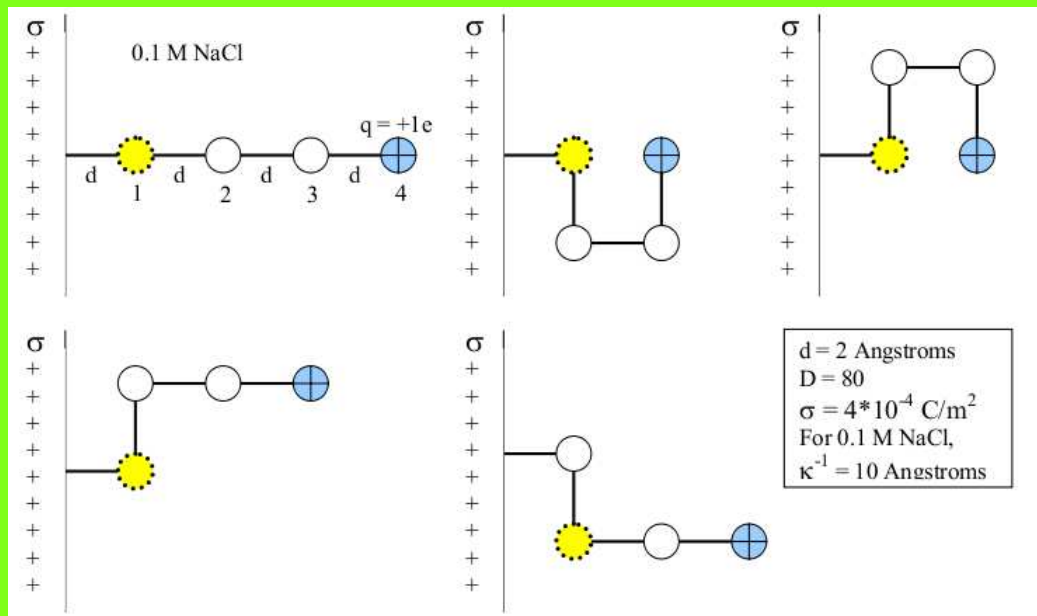
Since $Q = Ze$ and $q = ze$, where $Z = +20$ and $z = +2$ are the valences, then

$$\frac{\Delta G}{kT} = \frac{(20)(2)}{\left(1 + \frac{14 \text{ \AA}}{9.62 \text{ \AA}}\right)} \left(\frac{7.13 \text{ \AA}}{14 \text{ \AA}}\right) = 8.30 \quad \text{so} \quad \Delta G = 4.92 \frac{\text{kcal}}{\text{mol}}$$

$$(b) \quad \frac{\Delta G}{kT} = \frac{(20)(2)}{\left(1 + \frac{14 \text{ \AA}}{30.4 \text{ \AA}}\right)} \left(\frac{7.13 \text{ \AA}}{14 \text{ \AA}}\right) = 13.95 \quad \text{so} \quad \Delta G = 8.26 \frac{\text{kcal}}{\text{mol}}$$

14. Polymer on charged surface.

A polymer with a single positive charge at one end is attached to a uniformly charged sheet in a 0.1 M NaCl solution at the other end. It can take on the conformations shown. The distances, d , between model monomer beads is 2 Å.



The electric potential at bead 4 due to the shielded sheet is: $\psi(x) = \frac{\sigma}{\kappa\epsilon_n D} e^{-\kappa x}$, where $\sigma = 4 \times 10^{-4} \text{C/m}^2$, $D = 80$, and $\kappa = 10 \text{\AA}$.

Beads 1 and 4 have a favorable contact energy of $\epsilon = -2k_B T$, where $T = 300$ K. If the beads are not adjacent to each other, there is no contact energy.

- Compute the energy and density of states for each energy level of the above ensemble.
- What is the partition function for this polymer? Express your answers in terms of the energies computed above.
- Based on your partition function, what is the fraction of polymer in each state?
- Now assume that the system is moved to a lower dielectric medium, with $D = 20$, but still with 0.1 M NaCl. What is the fraction of polymer in the linear state when immersed in the new solvent? Explain why this fraction increased or decreased from the previous system.

- (a) The electric potential at bead 4 due to the shielded sheet is: $\psi(x) = \frac{\sigma}{\kappa\epsilon_0 D} e^{-\kappa x}$, so the electrostatic energy at distance x from the sheet is $U(x) = q \cdot \psi(x)$.

Linear polymer:

$$D(s) = 1$$

$$U(x) = \frac{e\sigma}{\kappa\epsilon_0 D} e^{-\kappa \cdot 4d}$$

$$U(x) = \frac{(1.6 \cdot 10^{-19} C)(4 \cdot 10^{-4} \frac{C}{m^2})(10^{-9} m) \frac{-8A}{10A}}{(8.85 \cdot 10^{-12} \frac{C}{V \cdot m})(80)} e^{\frac{-8A}{10A}}$$

$$= 9.04 \cdot 10^{-23} CV \cdot e^{-0.8} = 4.06 \cdot 10^{-23} J$$

Bent polymer:

$$D(s) = 2$$

$$U(x) = \frac{e\sigma}{\kappa\epsilon_0 D} e^{-\kappa \cdot 3d}$$

$$U(x) = 9.04 \cdot 10^{-23} CV \cdot e^{\frac{-6A}{10A}} = 4.96 \cdot 10^{-23} J$$

- (b) $Q = e^{-\frac{U(4d)}{k_B T}} + 2e^{-\frac{U(3d)}{k_B T}} + 2e^{-\frac{U(2d)}{k_B T} - 2}$
- $$= e^{-\frac{(4.06 \cdot 10^{-23} J)}{4.14 \cdot 10^{-21}}} + 2e^{-\frac{(4.96 \cdot 10^{-23} J)}{4.14 \cdot 10^{-21}}} + 2e^{-\frac{(6.06 \cdot 10^{-23} J)}{4.14 \cdot 10^{-21}} - 2}$$
- $$Q = 0.9902 + 1.9762 + 14.5634 = 17.5298$$

- (c) Fraction of polymer in each state:

$$f(\text{linear}) = \frac{e^{-\frac{U(4d)}{k_B T}}}{Q} = \frac{0.9902}{17.5298} = 0.0565$$

$$f(\text{bent}) = \frac{2e^{-\frac{U(3d)}{k_B T}}}{Q} = \frac{1.9762}{17.5298} = 0.1128$$

$$f(\text{U-shaped}) = \frac{2e^{-\frac{U(2d)}{k_B T} - 2}}{Q} = \frac{14.5634}{17.5298} = 0.8308$$

- (d) The dielectric constant changes from 80 to 20, so $D_{\text{new}} = \frac{D_{\text{old}}}{4}$

κ is proportional to $D^{-\frac{1}{2}}$, so $\kappa_{new} = 2 \cdot \kappa_{old} = 0.2 \text{ \AA} = 2 \cdot 10^9 \frac{1}{m} = \frac{1}{5 \cdot 10^{-10} m}$

New energy levels:

Linear polymer:

$$U(x) = \frac{e\sigma}{2\kappa\epsilon_0(\frac{D}{4})} e^{-2\kappa \cdot 4d}$$

$$U(x) = \frac{(1.6 \cdot 10^{-19} C)(4 \cdot 10^{-4} \frac{C}{m^2})(5 \cdot 10^{-10} m) \frac{-8 \text{ \AA}}{20 \text{ \AA}}}{(8.85 \cdot 10^{-12} \frac{C}{V \cdot m})(20)} e^{-0.4}$$

$$= 1.81 \cdot 10^{-22} CV \cdot e^{-0.4} = 1.21 \cdot 10^{-22} J$$

Bent polymer:

$$U(x) = \frac{e\sigma}{2\kappa\epsilon_0(\frac{D}{4})} e^{-2\kappa \cdot 3d}$$

$$U(x) = 1.81 \cdot 10^{-22} J \cdot e^{\frac{-6 \text{ \AA}}{20 \text{ \AA}}} = 1.34 \cdot 10^{-22} J$$

U-shaped polymer:

$$U(x) = \frac{e\sigma}{2\kappa\epsilon_0(\frac{D}{4})} e^{-2\kappa \cdot 2d} - 2k_B T$$

$$U(x) = 1.81 \cdot 10^{-22} J \cdot e^{\frac{-4 \text{ \AA}}{20 \text{ \AA}}} - 8.28 \cdot 10^{-21} J = -8.13 \cdot 10^{-21} J$$

$$Q = e^{-\frac{U(4d)}{k_B T}} + 2e^{-\frac{U(3d)}{k_B T}} + 2e^{-\frac{U(2d)}{k_B T} - 2}$$

$$= e^{-\frac{(1.21 \cdot 10^{-22} J)}{4.14 \cdot 10^{-21}}} + 2e^{-\frac{(1.34 \cdot 10^{-22} J)}{4.14 \cdot 10^{-21}}} + 2e^{-\frac{(1.48 \cdot 10^{-22} J)}{4.14 \cdot 10^{-21}} - 2}$$

$$= 0.9712 + 1.9363 + 14.2523 = 17.1598$$

The new fraction of polymer in the linear state:

$$f(\text{linear}) = \frac{e^{-\frac{U(4d, D_{new})}{k_B T}}}{Q_{new}} = \frac{0.9712}{17.1598} = 0.0566$$

The fraction of polymer in the linear state has increased slightly. There are two competing dielectric effects: (1) the decreased dielectric increases electrostatic repulsion between the surface and the charge and (2) charge shielding increases with decreased dielectric (since the Debye length depends on the dielectric), decreasing the electrostatic repulsion. Besides these effects nearly balancing each other out, the electrostatic energy is overpowered by the contact energy.

15. Salting a Protein.

A particular protein has a large net charge at low pH. Adding a salt stabilizes the folded or the unfolded state?

Salt stabilizes the folded state by shielding the charge.

16. Debye length.

What is the Debye length for a 0.01 M solution of magnesium sulfate ($MgSO_4$), at $T = 300 \text{ K}$?

$$\begin{aligned}
\kappa^2 &= \frac{2(ze)^2 n_{\infty} \mathcal{N}}{D \epsilon_0 R T} \\
&= 2 \cdot 4\pi (1.386 \cdot 10^{-4} \frac{Jm}{mol}) (0.01 \frac{mol}{L}) (10^3 \frac{L}{m^3}) (\frac{6.022 \cdot 10^{23} \frac{molecules}{mol}}{80(8.314 \frac{J}{K \cdot mol})(300K)}) \\
\kappa^2 &= 0.001078 \cdot 10^{20} \frac{1}{m^2} \\
\frac{1}{\kappa} &= 3.046 \cdot 10^{-9} = 3.046 nm
\end{aligned}$$