

Solution to Basic [Exercise 2.1-4](#) "Derive the Formula for the Vacancy Equilibrium Concentration"

Illustration

First we need to determine the number of possibilities P_n to arrange n vacancies in a crystal of N atoms

- This is most easily done by constructing a table and look at the cases $n = 1$, $n = 2$, etc. until it becomes obvious what the general law will be

$n (= i)$	$p_n =$	Comment
1	N	All N places are available
2	$\frac{N \cdot (N - 1)}{2}$	N places for the first, only $N - 1$ places for the second vacancy. Exchanging both vacancies does not change the situation - we have to divide by 2
3	$\frac{N \cdot (N - 1) \cdot (N - 2)}{2 \cdot 3}$	Exchanging vacancies does not change the microstate, we have to divide by the number of all possible exchanges = $6 = 2 \cdot 3$.
<p>Make sure you understand the exchange argument: Here is the detailed reasoning: For vacancy No. 1 on place 1, you have <i>two possibilities</i>: No. 2 on place 2, No. 3 on place 3 <i>or</i> No 2 on place 3 and No. 3 on place 2. You can do the same thing for No. 2 on place 2 (exchange No. 1 and No. 3) and for No. 3 on place 3., so you have 2 options 3 times = 6 indistinguishable arrangements.</p>		
...	...	and so on
n	$\frac{N \cdot (N - 1) \cdot (N - 2) \cdot \dots \cdot (N - (n - 1))}{2 \cdot 3 \cdot \dots \cdot n}$	The obvious law for n vacancies. $\{1 \cdot 2 \cdot 3 \cdot \dots \cdot n\}$ of course is simply $n!$
n	$\frac{\{N \cdot (N - 1) \cdot (N - 2) \cdot \dots \cdot (N - (n - 1))\} \cdot \{(N - n)!\}}{n! \cdot \{(N - n)!\}}$	Extend the fraction by $(N - n)!$
n	$\frac{N!}{n! \cdot (N - n)!}$	Final result as used in subchapter 2.1 This is a standard expression in combinatorics and called the binomial coefficient .

The entropy of mixing thus is

$$S = k \cdot \ln \frac{N!}{n! \cdot (N - n)!} = k \cdot \left(\ln N! - \ln \{n! \cdot (N - n)!\} \right) = k \cdot \left(\ln N! - \ln n! - \ln (N - n)! \right)$$

- We now can write down the free enthalpy for a crystal of N atoms containing n vacancies

$$G(n) = n \cdot G_F - kT \cdot [\ln N! - \ln n! - \ln (N - n)!]$$

Now we need to find the minimum of $G(n)$ by setting $dG(n)/dn = 0$ and for that we must differentiate **factorials**. We will not do this directly (how would you do it?), but use suitable approximations as outlined in [subchapter 2.1](#).

- Mathematical approximation:** Use the simplest version of the [Stirling formula](#)

$$\ln x! \approx x \cdot \ln x$$

● **Physical approximation**, assuming that there are far fewer vacancies than atoms:

$$n \ll N \Rightarrow \frac{n}{N-n} \approx \frac{n}{N} = c_V = \text{concentration of vacancies}$$

Now all that is left is some trivial math (with some pitfalls, however!). The links lead to an appendix explaining some of the possible problems.

● Essentially we need to consider $dS(n)/dn$ using the Stirling formula

$$\frac{dS_n}{dn} = k \cdot \frac{d}{dn} \left(\ln N! - \ln n! - \ln (N-n)! \right) \approx k \cdot \frac{d}{dn} \left(N \cdot \ln N - n \cdot \ln n - (N-n) \cdot \ln (N-n) \right)$$

But we must not yet use the physical approximation, even so its tempting! With the formula for taking the derivative of products we obtain

$$\frac{dS_n}{dn} \approx k \cdot \left(\left(-\ln n - \frac{n}{n} \right) - \left(-\ln (N-n) + \frac{n-N}{N-n} \right) \cdot (-1) \right)$$

$$\frac{dS_n}{dn} \approx -k \cdot \left(\ln n + 1 - \ln (N-n) - 1 \right) = -k \cdot \left(\ln n - \ln (N-n) \right) = -k \cdot \ln \frac{n}{N-n}$$

● Now we can use the physical approximation and obtain

$$\frac{dS_n}{dn} \approx -k \cdot \ln c_V$$

Putting everything together gives

$$\frac{dG(n)}{dn} = 0 \Rightarrow G_F - T \cdot \frac{dS_n}{dn} = G_F + kT \cdot \ln c_V$$

● Reshuffling for c_V gives the final result

$$c_V = \exp \left(-\frac{G_F}{kT} \right)$$

● *q.e.d.*

What happens if we use better approximations of the [Stirling formula](#); e.g. $\ln x! \approx x \ln x - x$? Lets see:

- We start with the equation [from above](#) and write it out with the better formula. With the extra terms in red, we obtain

$$\frac{dS_n}{dn} = k \cdot \frac{d}{dn} \left((N \cdot \ln N - N) - (n \cdot \ln n - n) - [(N - n) \cdot \ln(N - n) - (N - n)] \right)$$

- After sorting out the signs, we have

$$\frac{dS_n}{dn} = k \cdot \frac{d}{dn} \left(N \cdot \ln N - N - n \cdot \ln n + n - [(N - n) \cdot \ln(N - n)] + N - n \right)$$

Everything in red cancels and we are back to our [old equation](#)

Appendix: Mathematical tricks and Pitfalls

Here are a few hints and problems in dealing with faculties and approximations.

Having $n \ll N$, i.e. $n/(N - n) \approx n/N = c_V =$ concentration of vacancies does *not* allow us to approximate $d/dn\{(N - n) \cdot \ln(N - n)\}$ by simply doing $d/dn\{N \cdot \ln N\} = 0$.

- This is so because d/dn gives the *change* of $N - n$ with n and that not only *might* be large even if $n \ll N$, but *will* be large because N is essentially constant and the only change comes from n .

The derivative of $u(x) \cdot v(x)$ is: $d/dx(u \cdot v) = du/dx \cdot v(x) + dv/dx \cdot u(x)$.

- The derivative of $\ln x$ is: $d/dx(\ln x) = 1/x$

Easy mistake: Don't forget the *inner derivative*, it produces an important *minus* sign:

$$\frac{d}{dn} \left(\ln(N - n) \right) = \frac{1}{N - n} \cdot \frac{d(N - n)}{dn} = \frac{1}{N - n} \cdot (-1)$$