Solution to Basic Exercise 2.1-4"Derive the Formula for the Vacancy Equilibrium Concentration"

Illustration

- First we need to determine the number of possibilites 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	$\dfrac{N \cdot (N-1)}{2}$	***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	$\dfrac{N \cdot (N-1) \cdot (N-2)}{2 \cdot 3}$	Exchanging vacancies does not change the microstate, we have to divide by the number of all possible exchanges **= 6 = 2 · 3**.
Make sure you understand the exchange argument: Here is the detailed reasoning: For vacancy No. **1** on place **1** , you have *two possibilities*: No. **2** on place **2**, No. **3** on place **3** *or* 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.		
...	...	and so on
n	$\dfrac{N \cdot (N-1) \cdot (N-2) \cdot .. \cdot (N-(n-1))}{2 \cdot 3 \cdot .... \cdot n}$	The obvious law for ***n*** vacancies. **{1· 2 · 3 · .... · n}** of course is simply n!
n	$\dfrac{\{N \cdot (N-1) \cdot (N-2) \cdot .. \cdot (N-(n-1))\} \cdot \{(N-n)!\}}{n! \cdot \{(N-n)!\}}$	Extend the fraction by **(*N* – *n*)!**
n	$\dfrac{N!}{n! \cdot (N-n)!}$	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

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

  - 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 **d*G*(*n*)/d*n* = 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:

$$n << N \Rightarrow$$

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

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 **d*S*(*n*)/d*n*** 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

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

- Reshuffling for c_V gives the final result

$$c_V = \exp -\frac{G_F}{kT}$$

- *q.e.d.*

- What happens if we use better approximations of the Stirling formula; e.g. **ln x!** ≈ **xln *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 $n << N$, 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/d*n*** gives the *change* of $N - n$ with n and that not only *might* be large even if $n << N$, 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:

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