

## Exercise 2.1-1

### Find the Mistake

Below, two pages from the [book](#) "Defects and Defect Processes (Hayes and Stoneham)" are shown.

- Can you find the mistake?
- Why is the result correct anyway?

Illustration

[Link to the Solution](#)

#### 3.1.1 Schottky and Frenkel Defects

Consider first a crystal of  $N$  atomic sites that, for simplicity, we may imagine to be a rare-gas crystal. We suppose there are no complications due to electronic or orientational degeneracy. Let  $g$  be the work necessary to create a single vacancy at constant temperature and pressure. We shall assume the vacancy concentration to be so low that defect-defect interactions can be ignored and hence that  $g$  is independent of the vacancy content. The free energy of the defective crystal contains three principal terms:

- (i) A term  $G_0$  corresponding to the perfect crystal.
- (ii) A term  $G_1 = ng$  coming from the work done in creating  $n$  vacancies.
- (iii) A term  $G_2 = -TS_{\text{config}}$  from the configurational entropy.

The concentration of vacancies at equilibrium is determined by the extremal condition

$$\frac{\partial G}{\partial n} = \frac{\partial}{\partial n} (G_0 + G_1 + G_2) = 0 \quad (3.2)$$

In our case  $G_0$  is independent of  $n$  by definition, and  $(\partial G_1/\partial n)$  is simply  $g$ . Equation (3.2) reduces to

$$g - T \frac{\partial}{\partial n} (S_{\text{config}}) = 0 \quad (3.3)$$

The configurational entropy term is obtained using a standard combinatorial method. The vacant lattice points can be arranged in  $P_L$  ways,

$$P_L = N! / [(N-n)!] \quad (3.4)$$

The configurational entropy is given by  $k_B \ln P_L$ , so that we have

$$S_{\text{config}} = k_B \ln \{N! / [(N-n)!]\} \quad (3.5)$$

We need  $T \partial S_{\text{config}} / \partial n$ , and this is found using Stirling's theorem that  $\ln(x!)$  tends to  $x \ln x$  at large  $x$ . If  $N$ ,  $(N - n)$  and  $n$  are all large, we find

$$T \frac{\partial S_{\text{config}}}{\partial n} = k_B T \ln \left( \frac{N-n}{n} \right) \quad (3.6)$$

If the defect concentration  $f \equiv n/N$  is small, the right-hand side of Equation (3.6) reduces to  $-k_B T \ln f$ . Collecting together the terms in  $\partial G / \partial n$  we find

$$g + k_B T \ln f = 0, \quad (3.7)$$

giving the fraction  $f$  of vacant sites as

$$f = \exp(-g/k_B T) \quad (3.8)$$

The fractional vacancy concentration depends exponentially on the Schottky formation energy  $g$ , and increases exponentially with increasing temperature.

Even the simple example discussed above raises some general points. The first concerns the reference energy state. Although for the simple Schottky defect this is the perfect crystal, there may be some choice in other cases. As an example we consider the energy of solution of an interstitial impurity, for example, oxygen, in a crystal. The reference state will be different when one considers the equilibrium of the crystal with a gas phase  $X_2$  and when one considers the equilibrium of the same crystal with a liquid compound  $MX$ . The two cases can be related, one to the other, but there is opportunity for confusion in analyzing published data on energies of solution.

A second point that can cause confusion arises in connection with Schottky disorder. The number of defects present in equilibrium will depend to a large extent on the energy required to create them. If one creates a vacancy by moving a bulk atom to a surface site, the energy will depend on the precise surface site, and hence the equilibrium would at first sight seem to depend on details such as the crystal habit. The resolution of this problem can be given in several forms. One way is to define Schottky disorder for an infinite crystal with no free surfaces or sinks. The vacancy is introduced by rearranging  $N$  atoms on  $N + 1$  sites, with a volume change if the process is to occur at constant pressure. It is the formation energy so defined that determines the equilibrium concentration of defects, in principle.

In many simple estimates of formation energies the experimental cohesive energy or the sublimation energy is required. It is here that problems could arise if the experiment measured some special property,