

CHAPTER 20

1. $U = nE_I$.

The number of ways to pick n from N is $N! / (N-n)!n!$. The number of ways to put n into $N' = n! / (N' - n)!n!$.

$$\text{Entropy } S = k_B \left(\log \frac{N!}{(N-n)!n!} + \log \frac{N'!}{(N'-n)!n!} \right).$$

$$\log \frac{N!}{(N-n)!n!} \approx N \log N - (N-n) \log (N-n) - n \log n$$

$$\log \frac{N'!}{(N'-n)!n!} \approx N' \log N' - (N'-n) \log (N'-n) - n \log n$$

$$\left(\frac{\partial F}{\partial n} \right)_T = \frac{\partial U}{\partial n} - T \frac{\partial S}{\partial n} = 0 \text{ in equilibrium; thus}$$

$$\begin{aligned} E_I &= k_B T \left(\log \frac{N-n}{n} + \log \frac{N'-n}{n} \right) \\ &= k_B T \log \frac{(N-n)(N'-n)}{n^2}. \text{ For } n \ll N, N', \end{aligned}$$

$$E_I = k_B T \log (NN'/n^2); \quad n = \sqrt{NN'} e^{-E_I/2k_B T}.$$

2. From (2), $n = N e^{-E/k_B T}$. For sodium, $N = 2.5 \times 10^{22}$ atoms/cm³. Thus

$$n \approx (2.5 \times 10^{22})(4 \times 10^{-18}) \approx 10^5 \text{ per cm}^3.$$

3a. $\hbar\omega = \frac{13.6}{\epsilon^2} \cdot \frac{3}{4}$ eV. From Table 10.3 we have $\epsilon(\infty) = 2.25$ for NaCl, whence $\hbar\omega = 2.0$ eV. The observed value quoted in Table 18.2 is 2.7 eV.

b. From Vol. I of Atomic energy levels, Circular 467 of the Nat. Bur. of Standards, 3p-3s = 16960 cm⁻¹ = 2.1 eV.