AA, BB, and AB neighbor pairs are all equal, the homogeneous solid solution will have a lower free energy than the corresponding mixture of crystallites of the pure elements. The free energy of the solid solution $A_{1-x}B_x$ is

$$F = F_0 - \tau\sigma(x) = F_0 + N\tau[(1-x)\log(1-x) + x\log x] , \tag{81}$$

which we must compare with

$$F = (1-x)F_0 + xF_0 = F_0 \tag{82}$$

for the mixture of A and B crystals in the proportion $(1-x)$ to x. The entropy of mixing is always positive—all entropies are positive—so that the solid solution has the lower free energy in this special case.

There is a tendency for at least a very small proportion of any element B to dissolve in any other element A, even if a strong repulsive energy exists between a B atom and the surrounding A atoms. Let this repulsive energy be denoted by U, a positive quantity. If a very small proportion $x \ll 1$ of B atoms is present, the total repulsive energy is xNU, where xN is the number of B atoms. The mixing entropy (80) is approximately

$$\sigma = -xN\log x \tag{83}$$

in this limit, so that the free energy is

$$F(x) = N(xU + \tau x\log x) , \tag{84}$$

which has a minimum when

$$\partial F/\partial x = N(U + \tau\log x + \tau) = 0 , \tag{85}$$

or

$$x = \exp(-1)\exp(-U/\tau). \tag{86}$$

This shows there is a natural impurity content in all crystals.

SUMMARY

1. The factor

$$P(\varepsilon_s) = \exp(-\varepsilon_s/\tau)/Z$$

is the probability of finding a system in a state s of energy ε_s when the system