Question

Ionic Crystals: (a) The ionization energy of potassium is 4.34 eV and the electron affinity of chlorine is 3.61 eV. The Madelung constant for the KCl structure is 1.748 and the distance between ions of opposite sign is 0.314 nm. On the basis of these data only, compute the cohesive energy of KCl. (b) The observed cohesive energy of KCl is 6.42 eV per ion pair. On the assumption that the difference between this figure and that obtained in a is due to the exclusion-principle repulsion, find the exponent n in the formula Br^{-n} for the potential energy arising from this source.

Solution

(a) The cohesive energy is the sum of the Coulomb energy (eq 10.1 in text) and the electron transfer energy

$$\begin{aligned} U_{coulomb} &= -\alpha \frac{e^2}{4\pi\epsilon_0 r_0} \qquad \text{where} \qquad \alpha = \text{Madelung const} \\ &= -1.748 \frac{(1.602 \times 10^{-19})^2 (8.988 \times 10^9)}{0.314 \times 10^{-9}} \\ &= -\frac{4.032 \times 10^{-28}}{0.314 \times 10^{-9}} \\ &= -1.284 \times 10^{-18}\, J \quad \text{or} \quad -8.02\, eV \end{aligned}$$

The electron transfer energy is the sum of the ionization energy of potassium plus the electron affinity of chlorine i.e 4.34 - 3.61 = 0.73 hence for KCl

$$U_{cohesive} = -8.02 + 0.73 = -7.29\, eV$$

On the basis of the given data the cohesive energy per ion pair for KCl is 7.29 eV.

(b) Since the measured value of the cohesive energy is 6.42 eV the difference due to exclusion-principle repulsion is 0.87 eV or $1.394 \times 10^{-19}\, J$, hence (eq 10.2 & eq 10.4)

$$\begin{aligned} U_{repulsive} &= \frac{B}{r^n} = \frac{\alpha e^2}{4\pi\epsilon_0 r_0 n} \\ n &= \frac{\alpha e^2}{4\pi\epsilon_0 r_0 (1.394 \times 10^{-19})} \\ &= \frac{1.748\,(1.602 \times 10^{-19})^2 (8.988 \times 10^9)}{(0.314 \times 10^{-9})(1.394 \times 10^{-19})} \\ &= \frac{4.032 \times 10^{-28}}{4.377 \times 10^{-29}} \\ &= 9.21 \end{aligned}$$

This gives a value of 9.21 for the exponent n in the approximate formula Br^{-n} for the contribution of the repulsive forces to the potential energy.