Example 6. Macrostate V, Table IIIA-2 was shown to have 36 microstates. The particle distribution is: $n_{1,V} = 1$, $n_{2,V} = 0$, $n_{3,V} = 1$, $n_{4,V} = 0$ and $n_{5,V} = 2$. The level degeneracies are $g_1 = 1$, $g_2 = g_3 = g_4 = 3$ and $g_5 = 1$. Verify that eqn. IIIA-7a yields 36 microstates for this macrostate.

$$W_V^{MB} = 4! \cdot \left[\left(\frac{1^1}{1!}\right) \left(\frac{3^0}{0!}\right) \left(\frac{3^1}{1!}\right) \left(\frac{3^0}{0!}\right) \left(\frac{1^2}{2!}\right)\right] = 4 \cdot 3 \cdot 2 \cdot 1 \cdot \left[\left(\frac{1}{1}\right)\left(\frac{1}{1}\right)\left(\frac{3}{1}\right)\left(\frac{1}{1}\right)\left(\frac{1}{2}\right)\right] = 36$$

Thus once the macrostate distributions have been determined (by trial and error), repeated application of eqn. IIIA-7 permits the determination of all I^* values of W_i with relative ease. The total number of microstates accessible in all I^* macrostates is

$$W = \sum_{i=1}^{I^*} W_i \qquad \text{(IIIA-8)}$$

The evaluation of W_i and W permit the evaluation of the required macrostate probabilities on the basis of a single underlying assumption.

THE EQUAL PROBABILITY AXIOM: ALL MICROSTATES ACCESSIBLE TO A SYSTEM UNDER GIVEN CONDITIONS ARE EQUALLY PROBABLE.

This assumption leads us directly to an understanding of the concept of equilibrium and ultimately to the formulation of the second law of thermodynamics (Unit IIIB). Thus the assumption is equivalent to a statement (but not a derivation) of the second law. Though the assumption seems credible, it is properly viewed as a postulate whose validity rests on the correspondence between predicted behavior and physical observations.

With the assumption that all microstates are equally probable, we can write the *probability of any macrostate*, p_i, as

$$p_i = \frac{W_i}{W} \qquad \text{(IIIA-9)}$$

This definition facilitates the determination of which macrostates will appear with greatest frequency in the system.

Exercise 7. Table IIIA-2 presents the 5 macrostate distributions for 4 particles in the 5 levels of Fig. IIIA-1 with a total energy of 36 B_o. If the particles are Boltzons, determine W_i for each of the 5 macrostates ($W_I = 36$, see Exmps. 5 and 6), as well as the total number of microstates, W, and the probability of each macrostate, p_i. The answers to this exercise are compiled in Table IIIA-3.

Exer. 7 concludes the development that results in the determination of Boltzon macrostate probabilities. The following section extends these methods to indistinguishable particles.

Ans. 5. I. $n_{3,I} = 3$; II. $n_{2,II} = 1$, $n_{3,II} = 1$, $n_{5,II} = 1$; III. $n_{1,III} = 1$, $n_{5,III} = 2$, all unlisted levels equal zero.