Then

$$S = \frac{U}{T} + Nk\ \ell n\ Z = \frac{2.07 \cdot 10^{-17}\ J}{323\ K} + 10^4\ part \cdot 1.38 \cdot 10^{-23}\ J/(part\ K) \cdot \ell n\ 714 = 97.0 \cdot 10^{-20}\ J/K$$

(b) the work interaction is adiabatic reversible, $đW_{rev} = \sum n_j d\varepsilon_j$. The distribution is unchanged $n_{j,b} = n_{j,a}$. Thus

$$U_b = n_1\varepsilon_{1,b} + n_2\varepsilon_{2,b} = 7 \cdot 10^3\ part \cdot 2.30 \cdot 10^{-21}\ J/part + 3 \cdot 10^3\ part \cdot 11.5 \cdot 10^{-21}\ J/part$$

$$= 5.06 \cdot 10^{-17}\ J$$

The work can be determined from the first law

$$U_b - U_a = \cancel{Q} + \cancel{W^i_{irr}} + W^i_{rev} = (5.06 - 2.07) \cdot 10^{-17} = 2.99 \cdot 10^{-17}\ J$$

The new temperature can be determined directly by writing the ratio

$$\frac{n_1}{n_2} = \left(\frac{Ng_1\ \exp\ (-\varepsilon_{1,b}/kT_b)}{Z}\right)\left(\frac{Z}{Ng_2\ \exp\ (-\varepsilon_{2,b}/kT_b)}\right)$$

or

$$T_b = \frac{\varepsilon_{2,b} - \varepsilon_{1,b}}{k\ \ell n\left(\frac{n_1 g_2}{n_2 g_1}\right)} = \frac{(11.5 - 2.3) \cdot 10^{-21}\ J/part}{1.38 \cdot 10^{-23}\ J/(part\ K) \cdot \ell n\left(\frac{7 \cdot 10^3\ part \cdot 10^3}{3 \cdot 10^3\ part \cdot 5 \cdot 10^2}\right)} = 433\ K$$

Exercise 3. Exmp. 3 considered work addition to "pump" a ruby laser into a lasing condition, viz., to achieve a negative temperature. Reexamine this problem and decide whether it was reversible or irreversible work that was added.

The solutions of the preceding problems depended on insight gained by making a microscopic distinction between a reversible work interaction, $đW^i_{rev} = \sum_j n_{j,i} d\varepsilon_j$, and that of irreversible work and/or heat, $đQ + đW^i_{irr} = \sum_j \varepsilon_j \delta n_{j,i}$. That this distinction also allows us to establish entropy change on a totally macroscopic basis is evident if one differentiates the microscopic expression for the equilibrium entropy for any of the three statistics, eqn. IIIB-13, 15 or 17. Among the resulting terms will be an expression for reversible work, eqn. IIIB-19. Identification of this term gives the desired connection between entropy change and other macroscopic variables, the *Gibbs Equation*.

$$dS = \frac{dU - đW^i_{rev}}{T} \qquad \text{(IIIB-20a)}$$

The derivation of the Gibbs Equation is completed for Boltzons in the following example. As a further example the same technique is employed in Appendix IIIB-B to complete the derivation for Fermions and, as an exercise, for Bosons. The result is the same for all three particle types. The Gibbs equation, which is our principal bridge between properties, is not restricted to a particular type of particle.