UNIT IIIC

MICROSCOPIC CALCULATION OF PERFECT GAS PROPERTIES

Precise thermodynamic calculations are dependent on the availability of accurate property data. Macroscopic property measurement to obtain these data has two serious drawbacks. One, accurate measurements are difficult, and therefore expensive. Two, the results are limited to the range covered by the measurements. Hence, many data points must be collected to cover a broad range. This unit introduces an alternative, microscopic, property determination procedure that overcomes both of these limitations.

The microscopic approach predicts properties on the basis of a model of individual particle behavior. Each model requires as input certain *particle characteristics*, e.g., mass, moment of inertia, the effective spring constant of the molecular bonds, etc. These parameters are *inferred* from measurement, usually from the emission spectra of the substance. Since the parameters are molecular constants, a single set is sufficient for each substance, and the analytical relationship between the model and the properties constitutes an extrapolation over a range of thermodynamic states. Thus the microscopic method doesn't simply produce required data. Its requirement that a molecular model be selected provides valuable understanding of how and why properties vary and when they can be expected to be constant. This perception can contribute significantly to engineering judgement.

In this unit we use the microscopic procedure to predict the properties of independent particle molecular gases. We will find that when gaseous particles are independent they fall within the perfect gas region. Further, gaseous system particles are indistinguishable. They obey either Bose-Einstein or Fermi-Dirac statistics depending upon whether they have an even or an odd number of subatomic components. In general, the properties of Bosons and Fermions are distinct (Unit IIID). But there is an asymptotic limit in which the fundamental basis of their difference, the Pauli exclusion principle (Unit IIIA), is inconsequential. In this limit the properties of Bosons and Fermions are the same. We will see below that for gases whose particles are atoms or molecules (as opposed to electrons or electromagnetic and acoustic waves) the limit is satisfied under almost all achievable conditions. Therefore, this unit considers the properties of molecular perfect gases only in the indistinguishable limit.

I. THE INDISTINGUISHABLE LIMIT

In Unit IIIB we developed the equilibrium distribution function for the distinguishable particles, Boltzons, as well as for the indistinguishable Fermions and Bosons