UNIT IIIC

MICROSCOPIC CALCULATION OF PERFECT GAS PROPERTIES

Statistical thermodynamics is a powerful tool for the determination of thermodynamic properties. The general technique requires selection of a model that describes the behavior of particles composing the system. Statistical procedures are then employed to predict thermodynamic properties. In this unit, we illustrate general techniques through application to molecular gas models. The numerical values of properties obtained by these procedures are of extreme practical significance. Equally important, however, is the physical insight provided by the form of the results and an understanding of the models upon which they are based.

Objectives

Upon concluding the unit the student should be able to:

1. Describe the indistinguishable limit and its significance in simplifying property determinations. Specify whether a given substance satisfies the indistinguishable limit at a specified thermodynamic state.

2. Differentiate between internal and external energy modes. Specify the relationship between the properties of each separate mode and those of the system as a whole.

3. Define the characteristic temperature for a model whose energy levels are specified as an analytic function.

4. Write the series definition of the partition function for a mode. Specify appropriate approximations for a mode partition function in the high- and low-temperature limits.

5. Derive an expression for a specified property from a given analytic expression for a mode's partition function.

6. Choose the correct number and types of modes for a specified molecule. Write an expression for its total properties and evaluate them at a specified state.

Supplementary References

1. Sonntag, R. E., and Van Wylen, G. J., Introduction to Thermodynamics: Classical and Statistical, Wiley (1971). Sects. 19.1 to 19.9 with Exmps. 19.1 to 19.7, and Exers. 19.1 to 19.35. Similar to this unit. A good supplement. Also, Chapter 18 provides a much more thorough treatment of the quantum mechanical principles underlying statistical mechanics with emphasis on the models employed in this unit.

2. Wark, K., Thrmodynamics, Second Ed., McGraw-Hill (1971). Sects. 10-7 to 10-15 with Exmps. 10-1 to 10-2 and Exers. 10-6 to 10-35. A brief but clear treatment that excludes polyatomic gases.

3. Holman, J. P., Thermodynamics, Second Ed., McGraw-Hill (1974). Sects. 8.2 to 8.5 with Exmps. 8-1 and 8-2 and Exers. 8-1 to 8-3, 8-8 to 8-13 and 8-16. Excludes polyatomic gases. Quite brief, a quick overview.