11.10: The Nature of Hypothetical States

It is worthwhile to call attention to some important aspects of this development. The hypothetical ideal gas standard state is a wholly theoretical construct. We create this "substance" only because it is convenient to have a name for the "unreal" state of substance A, whose Gibbs free energy we have denoted as $G_A^o\left(HIG^o\right) = \Delta_f G_A^o\left(HIG^o\right)$. We have developed procedures for calculating $\Delta_f G_A^o\left(HIG^o\right)$ from the properties of the corresponding real gas. Given the properties of real gas A, these procedures determine $\Delta_f G_A^o\left(HIG^o\right)$ uniquely. $\Delta_f G_A^o\left(HIG^o\right)$ is a useful quantity; the calculation of $\Delta_f G_A^o\left(HIG^o\right)$ is "real" even though the substance it putatively describes is not.

Other hypothetical states are frequently useful. Problem 8 in this chapter considers a hypothetical liquid state of methanol at 500 K and 1 atm—conditions at which the real substance is a gas. Alternative approximations enable us to calculate the Gibbs free energy of this hypothetical state in different ways. The results have predictive value. Not surprisingly, however, the alternative approximations produce Gibbs free energy values whose quantitative agreement is poor. Were it useful to do so, we could select one particular approximation and define the Gibbs free energy of the hypothetical superheated liquid methanol to be the value produced using that approximation. This would not make the superheated liquid methanol any more real, but it would uniquely define the Gibbs free energy of the hypothetical substance.

Later in our development, we create other hypothetical reference states. As for the hypothetical ideal gas standard state, we specify unique ways to calculate the properties of these hypothetical states from measurements that we can make on real systems.