

3.11: Absolute Entropy

By the Lewis and Randall statement of the third law, the entropy of a substance that forms a perfect crystal is identically equal to zero at absolute zero. Much as the ideal gas temperature scale has a natural zero at the temperature at which the volume extrapolates to zero, a perfect crystalline substance has a natural zero of entropy at this same temperature. We can choose a non-zero value for the absolute zero of temperature. The Centigrade scale is based on such a choice. However, for thermodynamic purposes, any such choice is much less convenient. Similarly, we could choose arbitrary values for the entropies of the elements at the absolute zero of temperature. The entropy of a perfect crystalline substance at absolute zero would then be the sum of the entropies of its constituent elements. (See problem 5.) However, choosing non-zero values proves to be much less convenient.

Given the entropy of a substance at absolute zero, its entropy at any higher temperature can be calculated from the entropy changes that occur as the substance is warmed to the new temperature. At the very lowest temperatures, this entropy change is calculated by integrating C_P/T , using Debye's theoretical relationship, $C_P = AT^3$; A is obtained from the value of C_P at the lowest temperature for which an experimental value of C_P is available. In temperature ranges where experimental heat capacity data are available, the entropy change is obtained by integration using these data.

Phase changes are isothermal and reversible. Where the substance undergoes phase changes, the contribution that the phase change makes to the entropy of the substance is equal to the enthalpy change for the phase change divided by the temperature at which it occurs.

At any given temperature, the entropy value that is obtained in this way is called the substance's **absolute entropy** or its **third-law entropy**. When the entropy value is calculated for one mole of the substance in its standard state, the resulting absolute entropy is called the **standard entropy**. The standard entropy is usually given the symbol S° . It is usually included in compilations of thermodynamic data for chemical substances.

We write $S_A^\circ(T)$ to indicate the absolute entropy of substance A in its standard state at temperature T . $S_A^\circ(T)$ is the entropy of the substance in its standard state at absolute zero plus the entropy increase that occurs as the substance changes reversibly to its standard state at T . So long as substance A forms a perfect crystal at absolute zero, $S_A^\circ(T)$ is the difference between its molar entropy at T and its molar entropy at absolute zero—as calculated from heat capacity and phase-change enthalpy data.

If substance A does not form a perfect crystal at absolute zero, the true value of $S_A^\circ(T)$ exceeds the calculated value. The excess is the molar entropy of the imperfect crystal at absolute zero. We observe the discrepancy when measured values, at T , of entropies of reactions that involve A fail to agree with those calculated using the incorrect value of $S_A^\circ(T)$.

In Section 11.2 we note that many tables of thermochemical properties present “absolute enthalpy” data for chemical substances. An absolute enthalpy is the difference between the enthalpies of a substance at two different temperatures, but the reference temperature is not absolute zero. In Section 6.4 and Section 6.5, we introduce enthalpy standard states and the standard enthalpy of formation of substance A at temperature T , which we designate as $\Delta_f H_A^\circ(T)$. We define the standard enthalpy of formation of any element at any temperature to be zero. In Section 8.6, we find that the enthalpy difference between reactants in their standard states and products in their standard states is readily calculated from the standard enthalpies of formation of the participating substances. As illustrated in Figure 8-2, this calculation is successful because it utilizes an isothermal cycle which begins and ends in a common set of elements, all of which are at the same temperature.

We can also define the standard entropy of formation of any substance to be the difference between its standard entropy, $S_A^\circ(T)$, and those of its pure constituent elements in their standard states at the same temperature. This definition is embedded in the Lewis and Randall statement of the third law. For example, the standard entropy of formation of water at 400 K is the difference

$$\begin{aligned}\Delta_f S^\circ(H_2O, 400\text{ K}) &= \Delta S^\circ(H_2O, 400\text{ K}) \\ &\quad - \Delta S^\circ(H_2, 400\text{ K}) - \frac{1}{2} \Delta S^\circ(O_2, 400\text{ K})\end{aligned}$$

Because of this definition, the standard entropy of formation of an element in its standard state is zero. We can calculate the standard entropy change for any reaction, $\Delta_r S^\circ(T)$, either as the difference between the standard entropies of formation (the $\Delta_f S^\circ(T)$ values) of the reactants and products or as the difference between their standard entropies (the $S_A^\circ(T)$ values). Either calculation is successful because it begins and ends with a common set of elements, all of which are at the same temperature. When we compute $\Delta_r S^\circ(T)$ using values of $S_A^\circ(T)$ for the reactants and products the reference temperature for the elements is absolute zero. When we compute $\Delta_r S^\circ(T)$ using values of $\Delta_f S^\circ(T)$ for the reactants and products, the reference temperature is T .

Given $\Delta_f H^\circ(T)$ and $\Delta_f S^\circ(T)$, the standard Gibbs free energy of formation is immediately obtained from $\Delta_f G^\circ(T) = \Delta_f H^\circ(T) - T\Delta_f S^\circ(T)$. For any element at any temperature, we have $\Delta_f H^\circ = 0$ and $\Delta_f S^\circ = 0$; it follows that the standard Gibbs free energy of formation of an element in its standard state is zero. Tables of thermodynamic data usually give values for $\Delta_f H^\circ$, $\Delta_f G^\circ$, and S° . (A set of standard entropies contains the same information as the corresponding set of entropies of formation. Entropies of formation are seldom tabulated. If $\Delta_f S^\circ$ is needed, it can be calculated either from $\Delta_f H^\circ$ and $\Delta_f G^\circ$ or from the absolute entropies of the substance and the elements from which it is formed.)

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