

6.2: Molar Entropies

With the convention that the entropy of a pure, perfectly-ordered crystalline solid at zero kelvins is zero, we can establish the third-law value of the molar entropy of a pure substance at any temperature and pressure. Absolute values of S_m are what are usually tabulated for calculational use.

6.2.1 Third-law molar entropies

Suppose we wish to evaluate the entropy of an amount n of a pure substance at a certain temperature T' and a certain pressure. The same substance, in a perfectly-ordered crystal at zero kelvins and the same pressure, has an entropy of zero. The entropy at the temperature and pressure of interest, then, is the entropy change $\Delta S = \int_0^{T'} \dot{dq}/T$ of a reversible heating process at constant pressure that converts the perfectly-ordered crystal at zero kelvins to the state of interest.

Consider a reversible isobaric heating process of a pure substance while it exists in a single phase. The definition of heat capacity as \dot{dq}/dT (Eq. 3.1.9) allows us to substitute $C_p dT$ for \dot{dq} , where C_p is the heat capacity of the phase at constant pressure.

If the substance in the state of interest is a liquid or gas, or a crystal of a different form than the perfectly-ordered crystal present at zero kelvins, the heating process will include one or more equilibrium phase transitions under conditions where two phases are in equilibrium at the same temperature and pressure (Sec. 2.2.2). For example, a reversible heating process at a pressure above the triple point that transforms the crystal at 0 K to a gas may involve transitions from one crystal form to another, and also melting and vaporization transitions.

Each such reversible phase transition requires positive heat q_{trs} . Because the pressure is constant, the heat is equal to the enthalpy change (Eq. 5.3.8). The ratio q_{trs}/n is called the molar heat or molar enthalpy of the transition, $\Delta_{\text{trs}}H$ (see Sec. 8.3.1). Because the phase transition is reversible, the entropy change during the transition is given by $\Delta_{\text{trs}}S = q_{\text{trs}}/nT_{\text{trs}}$ where T_{trs} is the transition temperature.

With these considerations, we can write the following expression for the entropy change of the entire heating process:

$$\Delta S = \int_0^{T'} \frac{C_p}{T} dT + \sum \frac{n\Delta_{\text{trs}}H}{T_{\text{trs}}} \quad (6.2.1)$$

The resulting operational equation for the calculation of the *molar* entropy of the substance at the temperature and pressure of interest is

$$S_m(T') = \frac{\Delta S}{n} = \int_0^{T'} \frac{C_{p,m}}{T} dT + \sum \frac{\Delta_{\text{trs}}H}{T_{\text{trs}}} \quad (6.2.2)$$

(pure substance,
constant p)

where $C_{p,m} = C_p/n$ is the molar heat capacity at constant pressure. The summation is over each equilibrium phase transition occurring during the heating process.

Since $C_{p,m}$ is positive at all temperatures above zero kelvins, and $\Delta_{\text{trs}}H$ is positive for all transitions occurring during a reversible heating process, the molar entropy of a substance is *positive* at all temperatures above zero kelvins.

The heat capacity and transition enthalpy data required to evaluate $S_m(T')$ using Eq. 6.2.2 come from calorimetry. The calorimeter can be cooled to about 10 K with liquid hydrogen, but it is difficult to make measurements below this temperature. Statistical mechanical theory may be used to approximate the part of the integral in Eq. 6.2.2 between zero kelvins and the lowest temperature at which a value of $C_{p,m}$ can be measured. The appropriate formula for nonmagnetic nonmetals comes from the Debye theory for the lattice vibration of a monatomic crystal. This theory predicts that at low temperatures (from 0 K to about 30 K), the molar heat capacity at constant volume is proportional to T^3 : $C_{V,m} = aT^3$, where a is a constant. For a solid, the molar heat capacities at constant volume and at constant pressure are practically equal. Thus for the integral on the right side of Eq. 6.2.2 we can, to a good approximation, write

$$\int_0^{T'} \frac{C_{p,m}}{T} dT = a \int_0^{T''} T^2 dT + \int_{T''}^{T'} \frac{C_{p,m}}{T} dT \quad (6.2.3)$$

where T'' is the lowest temperature at which $C_{p,m}$ is measured. The first term on the right side of Eq. 6.2.3 is

$$a \int_0^{T''} T^2 dT = (aT^3/3)|_0^{T''} = a(T'')^3/3 \quad (6.2.4)$$

But $a(T'')^3$ is the value of $C_{p,m}$ at T'' , so Eq. 6.2.2 becomes

$$S_m(T') = \frac{C_{p,m}(T'')}{3} + \int_{T''}^{T'} \frac{C_{p,m}}{T} dT + \sum \frac{\Delta_{\text{trs}}H}{T_{\text{trs}}} \quad (6.2.5)$$

(pure substance,
constant p)

In the case of a metal, statistical mechanical theory predicts an electronic contribution to the molar heat capacity, proportional to T at low temperature, that should be added to the Debye T^3 term: $C_{p,m} = aT^3 + bT$. The error in using Eq. 6.2.5, which ignores the electronic term, is usually negligible if the heat capacity measurements are made down to about 10 K.

We may evaluate the integral on the right side of Eq. 6.2.5 by numerical integration. We need the area under the curve of $C_{p,m}/T$ plotted as a function of T between some low temperature, T'' , and the temperature T' at which the molar entropy is to be evaluated. Since the integral may be written in the form

$$\int_{T''}^{T'} \frac{C_{p,m}}{T} dT = \int_{T=T''}^{T=T'} C_{p,m} d \ln(T/K) \quad (6.2.6)$$

we may also evaluate the integral from the area under a curve of $C_{p,m}$ plotted as a function of $\ln(T/K)$.

Ideally, the molar entropy values obtained by the calorimetric (third-law) method for a gas should agree closely with the values calculated from spectroscopic data. Table 6.1 shows that for some substances this agreement is not present. The table lists values of S_m° for ideal gases at 298.15 K evaluated by both the calorimetric and spectroscopic methods. The quantity $S_{m,0}$ in the last column is the difference between the two S_m° values, and is called the molar *residual entropy*.

In the case of HCl, the experimental value of the residual entropy is comparable to its uncertainty, indicating good agreement between the calorimetric and spectroscopic methods. This agreement is typical of most substances, particularly those like HCl whose molecules are polar and asymmetric with a large energetic advantage of forming perfectly-ordered crystals.

The other substances listed in Table 6.1 have residual entropies that are greater than zero within the uncertainty of the data. What is the meaning of this discrepancy between the calorimetric and spectroscopic results? We can assume that the true values of S_m° at 298.15 K are the *spectroscopic* values, because their calculation assumes the solid has only one microstate at 0 K, with an entropy of zero, and takes into account all of the possible accessible microstates of the ideal gas. The *calorimetric* values, on the other hand, are based on Eq. 6.2.2 which assumes the solid becomes a perfectly-ordered crystal as the temperature approaches 0 K.

The calorimetric values in Table 6.1 were calculated as follows. Measurements of heat capacities and heats of transition were used in Eq. 6.2.2 to find the third-law value of S_m for the vapor at the boiling point of the substance at $p = 1$ atm. This calculated value for the gas was corrected to that for the ideal gas at $p = 1$ bar and adjusted to $T = 298.15$ K with spectroscopic data.

The conventional explanation of a nonzero residual entropy is the presence of random rotational orientations of molecules in the solid at the lowest temperature at which the heat capacity can be measured, so that the crystals are not perfectly ordered. The random structure is established as the crystals form from the liquid, and becomes frozen into the crystals as the temperature is lowered below the freezing point. This tends to happen with almost-symmetric molecules with small dipole moments which in the crystal can have random rotational orientations of practically equal energy. In the case of solid H_2O it is the arrangement of intermolecular hydrogen bonds that is random. Crystal imperfections such as dislocations can also contribute to the residual entropy. If such crystal imperfection is present at the lowest experimental temperature, the calorimetric value of S_m° for the gas at 298.15 K is the molar entropy increase for the change at 1 bar from the imperfectly-ordered solid at 0 K to the ideal gas at 298.15 K and the residual entropy $S_{m,0}$ is the molar entropy of this imperfectly-ordered solid.

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