

12.9: Absolute Entropy

We can, of course, calculate the molar entropy of a substance at some temperature provided that we define the entropy at a temperature of absolute zero to be zero. By way of example, assuming that the molar entropy of hydrogen at 0 K is zero, calculate the absolute entropy of a kmole of H₂ gas at a temperature of 25°C (298.15 K) and a pressure of one atmosphere. We can do this in five stages, as follows. You will find it helpful to sketch these stages on a drawing similar to figure VI.5.

1. Heat the solid hydrogen from 0 K to 13.95 K at a pressure of 7173 Pa. (That's the triple point.) The increase in entropy is $\int C_P d(\ln T)$. Assuming that we know C_P as a function of temperature in this range, that comes to $2080 \text{ J K}^{-1} \text{ kmole}^{-1}$.
2. Liquefy it at the same temperature and pressure. The molar latent heat of fusion is $117000 \text{ J kmole}^{-1}$. Increase in entropy = $117000/13.95 = 8400 \text{ J K}^{-1} \text{ kmole}^{-1}$.
3. Vaporize it at the same temperature and pressure. The molar latent heat of vaporization is $911000 \text{ J kmole}^{-1}$. Increase in entropy = $911000/13.95 = 65300 \text{ J K}^{-1} \text{ kmole}^{-1}$.
4. Increase temperature to 298.15 K at constant pressure. See equation 12.9.3. The increase in entropy is $\int C_P d(\ln T)$. Assuming that we know C_P as a function of temperature in this range, that comes to $70000 \text{ J K}^{-1} \text{ kmole}^{-1}$.
5. Increase pressure to 1 atm = $1.013 \times 10^5 \text{ Pa}$ at constant temperature. See equation 12.9.4, from which we see that there is a *decrease* of entropy equal to $R \ln(P_2/P_1) = 8314 \ln(1.013 \times 10^5 / 7173) = 22000 \text{ J K}^{-1} \text{ kmole}^{-1}$.

Hence, taking the entropy to be zero at 0 K, the required entropy is $124000 \text{ J K}^{-1} \text{ kmole}^{-1}$.

Now that we have calculated the absolute entropy at a given temperature and pressure, we can calculate the increase in the Helmholtz and Gibbs functions from equations 12.9.9 and 12.9.11. But this leaves us in a rather uncomfortable position. After all, all we have done in this example is to calculate the *increase* in entropy as we took the sample up to 25 °C and 1 atmosphere – we haven't *really* calculated the *absolute* entropy. The entropy appearing in equations 12.9.9 and 12.9.11 is surely the *absolute* entropy, and we cannot calculate this unless we know the entropy at $T = 0 \text{ K}$. This slight puzzle will remain with us until Chapter 16, when we meet Nernst's Heat Theorem and the Third Law of Thermodynamics.

Many of the examples of thermodynamical calculations have hitherto involved PdV work in a system in which the working substance has been an ideal gas. Let us now look at two entirely different situations, both involving non- PdV work. Let us look at charging a battery, and creating new surface by distorting a spherical drop of liquid.

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