5.4: Calculating Entropy Changes

Entropy changes are fairly easy to calculate so long as one knows initial and final state. For example, if the initial and final volume are the same, the entropy can be calculated by assuming a reversible, isochoric pathway and determining an expression for $\frac{dq}{T}$. That term can then be integrated from the initial condition to the final conditions to determine the entropy change.

Isothermal Changes

If the initial and final temperatures are the same, the most convenient reversible path to use to calculate the entropy is an isothermal pathway. As an example, consider the isothermal expansion of an ideal gas from V_1 to V_2. As was derived in Chapter 3,

$$dq = nRT\frac{dV}{V}$$

So dq/T is given by

$$\frac{dq}{T} = nR\frac{dV}{V}$$

and so

$$\Delta S = \int \frac{dq}{T} = nR\int_{V_1}^{V_2} \frac{dV}{V} = nR\ln\left(\frac{V_2}{V_1}\right) \tag{5.4.1}$$

> ✔ **Example 5.4.1: Entropy Change for a Gas Expansion**
>
> Calculate the entropy change for 1.00 mol of an ideal gas expanding isothermally from a volume of 24.4 L to 48.8 L.
>
> **Solution**
> Recognizing that this is an isothermal process, we can use Equation 5.4.1
>
> $$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$
> $$= (1.00\,mol)(8.314 J/(mol\,K))\ln\left(\frac{44.8\,L}{22.4\,L}\right)$$
> $$= 5.76\,J/K$$

Isobaric Changes

For changes in which the initial and final pressures are the same, the most convenient pathway to use to calculate the entropy change is an isobaric pathway. In this case, it is useful to remember that

$$dq = nC_p dT$$

So

$$\frac{dq}{T} = nC_p\frac{dT}{T}$$

Integration from the initial to final temperature is used to calculate the change in entropy. If the heat capacity is constant over the temperature range

$$\int_{T_1}^{T_2} \frac{dq}{T} = nC_p\int_{T_1}^{T_2} \frac{dT}{T} = nC_p\ln\left(\frac{T_2}{T_1}\right)$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral. For example, if C_p can be expressed as

$$C_p = a + bT + \frac{c}{T^2}$$

ΔS takes the form

$$\int_{T_1}^{T_2} \frac{dq}{T} = n \int_{T_1}^{T_2} \frac{a + bT + \frac{c}{T^2}}{T} \, dT$$

which simplifies to

$$\Delta S = n \int_{T_1}^{T_2} \left(\frac{a}{T} + bT + \frac{c}{T^3} \right) dT$$

or

$$\Delta S = n \left[a \ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) - \frac{c}{2}\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right) \right]$$

Isochoric Changes

Similarly to the cast of constant pressure, it is fairly simple to calculate ΔS. Since

$$dq = nC_V dt$$

$\dfrac{dq}{T}$ is given by

$$\frac{dq}{T} = nC_V \frac{dT}{T}$$

And so for changes over which C_V is independent of the temperature ΔS is given by

$$\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right)$$

Adiabatic Changes

The easiest pathway for which to calculate entropy changes is an adiabatic pathway. Since $dq = 0$ for an adiabatic change, then $dS = 0$ as well.

Phase Changes

The entropy change for a phase change at constant pressure is given by

$$\Delta S = \frac{q}{T} = \frac{\Delta H_{phase}}{T} \tag{5.4.2}$$

> ✔ **Example 5.4.2: Entropy Change for Melting Ice**
>
> The enthalpy of fusion for water is 6.01 kJ/mol. Calculate the entropy change for 1.0 mole of ice melting to form liquid at 273 K.
>
> **Solution**
> This is a phase transition at constant pressure (assumed) requiring Equation 5.4.2:
>
> $$\Delta S = \frac{(1\,mol)(6010\,J/mol)}{273\,K}$$
> $$= 22\,J/K$$

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