5.5: Comparing the System and the Surroundings

It is oftentimes important (for reasons that will be discussed in the next section) to calculate both the entropy change of the system as well as that of the surroundings. Depending on the size of the surroundings, they can provide or absorb as much heat as is needed for a process without changing temperature. As such, it is oftentimes a very good approximation to consider the changes to the surroundings as happening isothermally, even though it may not be the case for the system (which is generally smaller.)

> ✔ **Example 5.5.1**
>
> Consider 18.02 g (1.00 mol) of ice melting at 273 K in a room that is 298 K. Calculate DS for the ice, the surrounding room, and of the universe. (DH_{fus} = 6.01 kJ/mol)
>
> **Solution**
>
> For the process under constant pressure: $q_{ice} = -q_{room}$:
>
> $$q = n\Delta H_{fus} = (1.00\,mol)(6010\,J/mol) = 6010\,J$$
>
> For the ice:
>
> $$\Delta S_{ice} = \frac{q_{ice}}{T_{ice}} = \frac{6010\,J}{273\,K} = 22.0\,J/K$$
>
> For the room:
>
> $$\Delta S_{room} = \frac{q_{room}}{T_{room}} = \frac{-6010\,J}{298\,K} = -20.2\,J/K$$
>
> For the universe:
>
> $$\Delta S_{univ} = \Delta S_{ice} + \Delta S_{room}$$
> $$= 22.0\,J/K - 20.2\,J/K = 1.8\,J/K$$
>
> *Note*: ΔS_{univ} is positive, which is characteristic of a spontaneous change!

> ✔ **Example 5.5.2**
>
> A 10.0 g piece of metal (C = 0.250 J/g °C) initially at 95 °C is placed in 25.0 g of water initially at 15 °C in an insulated container. Calculate the final temperature of the metal and water once the system has reached thermal equilibrium. Also, calculate the entropy change for the metal, the water, and the entire system.
>
> **Solution**
>
> Heat will be transferred from the hot metal to the cold water. Since it has nowhere else to go, the final temperature can be calculated from the expression
>
> $$q_w = -q_m$$
>
> where q_w is the heat absorbed by the water, and q_m is the heat lost by the metal. And since
>
> $$q = mC\Delta T$$
>
> it follows that
>
> $$(25\,g)(4.184\,J/g\,°C))(T_f - 15\,°C) = -(10.0\,g)(0.250\,J/g\,°C))(T_f - 95\,J/g\,°C)$$
>
> A bit of algebra determines the final temperature to be:
>
> $$T_f = 16.9\,°C.$$
>
> To get the entropy changes, use the expression:
>
> $$\Delta S = mC_p \ln\left(\frac{T_f}{T_i}\right)$$

So, for the water:

$$\Delta S_{water} = (25\ g)(4.184\ J/g\,{}^\circ C))\ln\left(\frac{289.9\ K}{288\ K}\right)$$

$$= 0.689\ J/K$$

And for the metal:

$$\Delta S_{metal} = (10.0\ g)(0.250\ J/g\,{}^\circ C))\ln\left(\frac{289.9\ K}{368\ K}\right)$$

$$= -0.596\ J/K$$

For the system:

$$\Delta S_{sys} = \Delta S_{water} + \Delta S_{metal}$$

$$= 0.689\ J/K + -0.596\ J/K = 0.093\ J/K$$

Note: The total entropy change is positive, suggesting that this will be a spontaneous process. This should make some sense since one expects heat to flow from the hot metal to the cool water rather than the other way around. Also, note that the sign of the entropy change is positive for the part of the system that is absorbing the heat, and negative for the part losing the heat.

In summary, ΔS can be calculated for a number of pathways fairly conveniently.

Table 5.5.1: *Summary of different ways to calculate ΔS depending on the pathway.*

Pathway	$\Delta S_{sys} = \ln \dfrac{dQ_{rev}}{T_{sys}}$		$\Delta S_{surr} = \dfrac{q_{sys}}{T_{surr}}$
Adiabatic	0		
Isothermal	$\dfrac{q_{rev}}{T}$ and	$nR\ln\left(\dfrac{V_2}{V_1}\right)$*	
Isobaric	$mC_p\ln\left(\dfrac{T_f}{T_i}\right)$		$\Delta S_{surr} = \dfrac{q_{sys}}{T_{surr}}$
Isochoric	$mC_V\ln\left(\dfrac{T_f}{T_i}\right)$		
Phase Change	$\dfrac{\Delta H_{phase}}{T}$		
for an ideal gas.			

And

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}.$$

This calculation is important as ΔS_{univ} provides the criterion for spontaneity for which we were searching from the outset. This also suggests a new way to state the second law:

> *The entropy of the universe increases in any spontaneous change.*

If we think of "the direction of spontaneous" to be the natural direction of chance, we can see that entropy and the second law are tied inexorably with the natural direction of the flow of time. Basically, we can expect the entropy of the universe to continue to increase as time flows into the future. We can overcome this natural tendency to greater entropy by doing work on a system. This is why it requires such great effort, for example, to straighten a messy desk, but little effort for the desk to get messy over time.

> ### 📌 Clausius Inequality
>
> The Second Law can be summed up in a very simple mathematical expression called the *Clausius Inequality*.
>
> $$\Delta S_{universe} \geq 0$$
>
> which must be true for any spontaneous process. It is not the most convenient criterion for spontaneity, but it will do for now. In the next chapter, we will derive a criterion which is more useful to us as chemists, who would rather focus on the system itself rather than both the system and its surroundings. Another statement of the Clausius theorem is
>
> $$\oint \frac{dq}{T} \geq 0$$
>
> with the only condition of the left hand side equaling zero is if the system transfers all heat reversibly.

Contributors

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