A Reversible Process

An isobaric phase change at the phase change temperature is a great simple example of a reversible process. A pot filled with 400.0 g of water are boiled on a stove. In this scenario, we can consider the surroundings to be at the boiling temperature.

→ 22.2 moles $\Delta C_p = -42.09 \frac{J}{mol \cdot K}$

Find ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} for this process

$\Delta H^\ominus_{vap}(373\,K) = \Delta H^\ominus_{vap}(298) + \Delta C_p \cdot 75\,K$

$\Delta H^\ominus_{vap}(373\,K) = 44.01 \frac{kJ}{mol} + (-0.04209 \frac{kJ}{mol \cdot K}) \cdot 75\,K = 40.85 \frac{kJ}{mol}$

$q = 22.2\,moles \cdot 40.85 \frac{kJ}{mol} = 907\,kJ$

$\Delta S_{sys} = \frac{907\,kJ}{373\,K} = 2.43 \frac{kJ}{K}$ $\Delta S_{surr} = \frac{-907\,kJ}{373\,K} = -2.43 \frac{kJ}{K}$ $\Delta S_{univ} = \emptyset$

A Non-Spontaneous Process. . . which isn't (or, rather, which really *is* spontaneous)

A pot filled with 400.0 g left out 298 K may evaporate into the vapor phase given enough time. Find ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} for this phase change and show that it is non-spontaneous. (Remember that ΔH must be corrected by Kirchoff's law)

$\Delta H_{vap}(298\,K) = 44.01 \frac{kJ}{mol}$

$q_{real} = 22.2\,moles \cdot 44.01 \frac{kJ}{mol} = 977\,kJ$ $\Delta S_{surr} = \frac{-977\,kJ}{298\,K} = -3.28 \frac{kJ}{K}$

Model the process as heating to 373, vaporizing reversibly, and cooling the vapor to 298

$C_{p(l)} = 75.35 \frac{J}{mol \cdot K}$ $C_{p(g)} = 4R = 33.256 \frac{J}{mol \cdot K}$

$\Delta S_{sys} = \Delta S_{heating} + \Delta S_{vap} + \Delta S_{cooling}$

$\Delta S_{sys} = 22.2\,mol \cdot 75.35 \frac{J}{mol \cdot K} \cdot \ln\left(\frac{373\,K}{298\,K}\right) + 2.43 \frac{kJ}{K} + 22.2\,mol \cdot 33.256 \frac{J}{mol \cdot K} \cdot \ln\left(\frac{298\,K}{373\,K}\right) = 2.64 \frac{kJ}{K}$

$\Delta S_{univ} = -0.640 \frac{kJ}{K}$

And yet, you *know* that such a process will happen spontaneously in nature. . . at least, in Utah it will. What factor have we neglected, and how can we correct our calculations to include it?

All the above work assumes an isobaric phase change, i.e. that the water vapor has a pressure of 1 atm. That is true @ 373 K, but at 298 K, $P_{H_2O} = 0.0313$ atm

In a dry environment, humidity will be even lower, say 0.02 atm for example.

The water vapor will expand isothermally from 1 atm to 0.02 atm, or by 50×, ~~in both the real and reversible pathways. Real @ 298 K~~

$\Delta S_{expansion} = nR \ln\left(\frac{V_2}{V_1}\right) = 22.2\,moles \cdot 8.314 \frac{J}{mol \cdot K} \cdot \ln 50 = 722 \frac{J}{K}$, more than enough to make up the shortfall!

and $\Delta S_{univ} = +82 \frac{J}{K}$

p.s. @ 0.0313 atm, or 100% humidity for 298 K, $\Delta S_{exp} = 640 \frac{J}{K}$, perfectly matching the shortfall and giving $\Delta S_{univ} = \emptyset$. i.e. @ 100% humidity evaporation is reversible even below the normal boiling point!