

## Quiz 3.2 – Spontaneity

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## A Spontaneous Process

Consider the reaction:  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$ 

At 298 K, this reaction has  $\Delta H^\ominus = -483.64 \frac{\text{kJ}}{\text{mol}}$  and  $\Delta S^\ominus = -88.846 \frac{\text{J}}{\text{mol K}}$ . Use these data to find  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{sur}}$ , and  $\Delta S_{\text{univ}}$  for this reaction, and show that it is spontaneous under standard conditions

$$\Delta S_{\text{sys}} = -88.846 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S_{\text{sur}} = \frac{-\Delta H_{\text{sys}}}{T} = \frac{483,640 \frac{\text{J}}{\text{mol}}}{298 \text{ K}} = 1623 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$$\Delta S_{\text{univ}} = -88.846 \frac{\text{J}}{\text{mol K}} + 1623 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S_{\text{univ}} = 1534 \frac{\text{J}}{\text{mol K}}$$

Positive, so spontaneous

## Entropy on Astronomical Scales

The sun radiates heat from its surface at a temperature of 5,778 K. Some of this heat reaches the earth, where it is absorbed, and re-emitted at the average global temperature of about 15°C. The Earth's heat radiates away into space, which acts as a heat sink at 2.7 K (The temperature of the cosmic microwave background). The Earth's temperature is fairly constant, so we can assume the heat absorbed from the sun and the heat emitted into space are balanced. For a collection of photons,  $S = \frac{E}{T}$ , where  $T$  is the characteristic Black-body temperature based on the spectral profile of the photons. Find  $\Delta S_{\text{univ}}$  for each 1000 J of energy absorbed then re-emitted by the Earth.

$$\Delta S_{\text{absorbed}} = \frac{1000 \text{ J}}{5,778 \text{ K}} = 0.1731 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{emitted}} = \frac{1000 \text{ J}}{2.7 \text{ K}} = 3.704 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{univ}} = 3.299 \frac{\text{J}}{\text{K}}$$

## Conditions for spontaneity

In class we saw how  $\Delta H$  and  $\Delta S$  can determine the conditions under which a reaction will be spontaneous. However, that discussion only applied to isobaric processes. Fill out the table below to indicate the conditions under which isochoric processes are spontaneous

		$\Delta S$	
		+	-
$\Delta U$	+	At high temperatures	No temperature
	-	All temperatures	At low temperatures

### 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.

Find  $\Delta S_{sys}$ ,  $\Delta S_{surr}$ , and  $\Delta S_{univ}$  for this process

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

$$\Delta C_p = -42.09 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$\Delta H_{vap}^\ominus(373 \text{ K}) = \Delta H_{vap}^\ominus(298) + \Delta C_p \cdot 75 \text{ K}$$

$$\Delta H_{vap}^\ominus(373 \text{ K}) = 44.01 \frac{\text{kJ}}{\text{mol}} + (-0.04209 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}) \cdot 75 \text{ K} = 40.85 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta S_{sys} = \frac{907 \text{ kJ}}{373 \text{ K}} = 2.43 \frac{\text{kJ}}{\text{K}}$$

$$\Delta S_{surr} = \frac{-907 \text{ kJ}}{373 \text{ K}} = -2.43 \frac{\text{kJ}}{\text{K}}$$

$$\Delta S_{univ} = 0$$

### 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  $\Delta S_{sys}$ ,  $\Delta S_{surr}$ , and  $\Delta S_{univ}$  for this phase change and show that it is non-spontaneous. (Remember that  $\Delta H$  must be corrected by Kirchoff's law)

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

$$q_{\text{evap}} = 22.2 \text{ moles} \cdot 44.01 \frac{\text{kJ}}{\text{mol}} = 977 \text{ kJ}$$

$$\Delta S_{surr} = \frac{-977 \text{ kJ}}{298 \text{ K}} = -3.28 \frac{\text{kJ}}{\text{K}}$$

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

$$C_p(l) = 75.35 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

$$C_p(g) = 4R = 33.256 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

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

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

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

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,  $p_{H_2O} = 0.0313 \text{ atm}$

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 50x, via both the fast and reversible pathways.  $p_{\text{evap}} = 0.02 \text{ atm}$

$$\Delta S_{\text{expansion}} = nR \ln\left(\frac{V_2}{V_1}\right) = 22.2 \text{ moles} \cdot 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot \ln 50 = 722 \frac{\text{J}}{\text{K}}$$

More than enough to make up the shortfall!

p.s. @ 0.0313 atm, or 100% humidity for 298 K,  $\Delta S_{\text{exp}} = 640 \frac{\text{J}}{\text{K}}$ , perfectly matching the shortfall and giving  $\Delta S_{univ} = 0$ . i.e. @ 100% humidity, evaporation is reversible even below the normal boiling point!

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