THERMODYNAMICS

ENTROPY AND SPONTANEITY

CHEMISTRY 165 // SPRING 2020

DR. MIOY T. HUYNH | 2020

PRACTICE PROBLEM 1

Which of the following combinations of entropy changes is not possible?

— answer —

	ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	Possible?
(i)	<0	>0	>0	
(ii)	<0	<0	>0	
(iii)	>0	<0	>0	

PRACTICE PROBLEM 1

Which of the following combinations of entropy changes is not possible?

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For all three choices, the $\Delta S_{univ} > 0$, which means that all are spontaneous processes—this is the second law of thermodynamics.

Now, we can work through each combination to see if the following is true:

$$\Delta S_{\mathrm{sys}} + \Delta S_{\mathrm{surr}} = \Delta S_{\mathrm{univ}}$$
$$\Delta S_{\mathrm{sys}} + \Delta S_{\mathrm{surr}} > 0$$

	ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	Possible?
(i)	<0	>0	>0	Yes, if $\lvert\Delta S_{\mathrm{surr}}\rvert > \lvert\Delta S_{\mathrm{sys}}\rvert$.
(ii)	<0	<0	>0	No.
(iii)	>0	<0	>0	Yes, if $\lvert\Delta S_{\mathrm{surr}}\rvert < \lvert\Delta S_{\mathrm{sys}}\rvert$.

PRACTICE PROBLEM 2

$$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$$

(a) Predict the sign of $\Delta S°$.

(b) Calculate the $\Delta S°$ for the reaction using the following standard molar entropies ($S°$).

	NO (g)	O_2 (g)	NO_2 (g)
$S° \left(\frac{\mathrm{J}}{\mathrm{mol \cdot K}}\right)$	210.7	205.0	240.0

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— answer —

(a) First, recognize that entropy is a measure of the disorder of a system, so the greater the disorder, the greater the entropy. Because we are going from 3 moles of gaseous species in the reactants to only 2 moles of gaseous species in the products, the entropy (disorder) of the system decreases ($\Delta S < 0$).

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(b) $\Delta S^{o}_{\text{rxn}} = \sum n_{\text{prod}}\, S^{o}_{\text{prod}} - \sum n_{\text{react}}\, S^{o}_{\text{react}}$

$$= (2\ \text{mol NO}_2)\times\left(240.0\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right) - \left[(2\ \text{mol NO}_2)\times\left(210.5\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right) + (1\ \text{mol O}_2)\times\left(205.0\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)\right]$$

$$\Delta S^{o}_{\text{rxn}} = -146.0\,\frac{\text{J}}{\text{K}}$$

PRACTICE PROBLEM 3

The entropy change for a block of ice melting is 22.1 J/K and the surroundings transfer 6.00 kJ of heat to the system. Is this process spontaneous at 10.0 °C?

$$H_2O\ (s) \rightleftharpoons H_2O\ (l)$$

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First, realize that for a process to be spontaneous, the entropy change of the universe must be positive:

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{univ}} > 0$$

We are already given the entropy change of the system: $\Delta S_{\text{sys}} = 22.1\,\frac{\text{J}}{\text{K}}$.

Now we can find the entropy change of the surroundings, which can be related to the heat transfer.

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T}$$

$$= \frac{-6.00\ \text{kJ} \times \frac{1000\ \text{J}}{1\ \text{kJ}}}{(10.0 + 273.15)\text{K}}$$

$$\Delta S_{\text{surr}} = -21.1_9\,\frac{\text{J}}{\text{K}}$$

And finally we can find the entropy change of the universe to determine the process is spontaneous.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 22.1\,\frac{\text{J}}{\text{K}} + \left(-21.1_9\,\frac{\text{J}}{\text{K}}\right) = 0.9\,\frac{\text{J}}{\text{K}} > 0$$