

Spontaneity, Entropy, Free Energy (aka – more Thermodynamics)

Entropy

Define-

spontaneous change:

entropy:

standard molar entropy:

standard entropy of reaction:

1st law of thermodynamics:

2nd law of thermodynamics:

3rd law of thermodynamics:

Fill in or circle-

A chemical reaction proceeding toward _____ is an example of a(n) _____ change.

The total energy of the universe is _____.

Under a given set of conditions, if a change is spontaneous in one direction it is / is not spontaneous in the other.

A spontaneous reaction does / does not mean the reaction is instantaneous.

Examples of spontaneous reactions are _____, _____, _____, and _____.

The sign of ΔH _____ predict spontaneous change.

In thermodynamic terms, a change in the freedom of motion of particles in a system and in the dispersal of their energy of motion is a key factor determining the _____ of a spontaneous change.

Each quantized state of a system is called a _____. Every _____ has the same _____ at a given set of conditions.

A system with fewer microstates (smaller W) among which to spread its energy has _____ entropy. A system with more microstates (larger W) among which to spread its energy has _____ entropy.

Entropy, like internal energy (E) and enthalpy (H), is a _____ function.

Like any state function, ΔS_{sys} _____ 0 when its value increases during a change.

A gas is more / less ordered than a solid.

Writing ΔS expressions – Write ΔS_{sys} expressions for the following:

- a. $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$
- b. $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
- c. $\text{O}_2\text{N-NO}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

Predicting relative S° values of a system – Trends

1. Temperature changes:

2. Physical states and phase changes:

3. Dissolving a solid or a liquid:

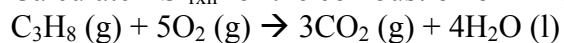
4. Dissolving a gas:

5. Atomic size or molecular complexity:

Examples:

1. Choose the one with the higher entropy in each of the following pairs and give a reason for your choice. (Assume constant pressure except in part e.)
 - a. 1 mol $\text{SO}_2(\text{g})$ or 1 mol $\text{SO}_3(\text{g})$
 - b. 1 mol $\text{CO}_2(\text{s})$ or 1 mol $\text{CO}_2(\text{g})$
 - c. 3 mol $\text{O}_2(\text{g})$ or 2 mol $\text{O}_3(\text{g})$
 - d. 1 mol $\text{KBr}(\text{s})$ or 1 mol $\text{KBr}(\text{aq})$
 - e. Seawater in midwinter at 2°C or in midsummer at 23°C
 - f. 1 mol $\text{CF}_4(\text{g})$ or 1 mol $\text{CCl}_4(\text{g})$

2. Calculate $\Delta S^\circ_{\text{rxn}}$ for the combustion of 1 mol of propane at 25°C:



$$S^\circ \text{ for } \text{C}_3\text{H}_8 = 269.9 \text{ J/mol K}$$

$$\text{O}_2 = 205.0 \text{ J/mol K}$$

$$\text{CO}_2 = 213.7 \text{ J/mol K}$$

$$\text{H}_2\text{O} = 69.9 \text{ J/mol K}$$

Relating entropy change to endothermic and exothermic reactions –

The second law dictates that _____ in the entropy of the system can occur only if _____ in the entropy of the surroundings outweigh them.

Fill in the signs: (<, >, or =)

For an exothermic change - $q_{\text{sys}} \quad 0 \quad q_{\text{surr}} \quad 0 \quad \Delta S_{\text{surr}} \quad 0$

For an endothermic change - $q_{\text{sys}} \quad 0 \quad q_{\text{surr}} \quad 0 \quad \Delta S_{\text{surr}} \quad 0$

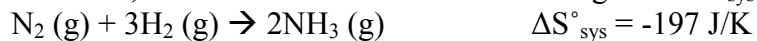
The change in entropy of the surroundings is directly related to a(n) _____ change in the heat of the system and _____ related to the temperature at which the heat is transferred.

Therefore:

And:

Example:

3. At 298 K, the formation of ammonia has a negative $\Delta S^\circ_{\text{sys}}$:



Calculate ΔS_{univ} and state whether the reaction occurs spontaneously at this temperature.

$$\Delta H \text{ of } \text{NH}_3 = -45.9 \text{ kJ/mol}$$

Summarizing exothermic and endothermic reactions –

1. For an exothermic reaction:

2. For an endothermic reaction:

Free Energy

Define-
free energy:

standard free energy of change:

standard free energy of formation:

Fill in the blanks or circle:

The free energy change, ΔG , is a measure of the _____ of a process and of the _____ available from it.

The _____ of ΔG tells if a reaction is _____.

$\Delta S_{\text{univ}} \underline{\quad} 0$ for a spontaneous process

$\Delta S_{\text{univ}} \underline{\quad} 0$ for a nonspontaneous process

$\Delta S_{\text{univ}} \underline{\quad} 0$ for a process at equilibrium

$T \Delta S_{\text{univ}} \underline{\quad} 0$ or $-T \Delta S_{\text{univ}} \underline{\quad} 0$ for a spontaneous process

Since $\Delta G = -T \Delta S_{\text{univ}}$:

$\Delta G \underline{\quad} 0$ for a spontaneous process

$\Delta G \underline{\quad} 0$ for a nonspontaneous process

$\Delta G \underline{\quad} 0$ for a process at equilibrium