



Thermodynamics & Chemical Energy

Understanding the exchanges of energy in chemical reactions is just as important as understanding their more physical aspects. There are several ways to measure energy in reactions. This worksheet explains the differences between them.

To begin, we measure overall chemical energy, from any source and in any form. Since the reactants have energy to start with, we're concerned with the difference in energy before and after a reaction. The symbol for "difference" is the capital Greek letter delta, Δ , so the symbol for difference in energy is ΔE . The unit for energy is the **joule (J)** or kilojoule (kJ). Differences in chemical energy are expressed in terms of the energy of the products relative to the energy of the reactants: if energy is gained during the reaction, ΔE is positive. If energy is released during the reaction, ΔE is negative.

Chemical energy is scaled so the coefficients in the reaction equation describe the numbers of moles involved. If ΔE for the reaction $2 \text{H}_2\text{O} \rightarrow 2 \text{H}_2 + \text{O}_2$ is -572 kJ , this means that when exactly 2 mol of water dissociates, 572 kJ of energy is released.

Energy exchanged in a reaction generally comes in two forms: heat energy and energy from compression or expansion of gases. After all, it takes effort to compress gas, and the sudden release of a compressed gas can cause a lot of damage. The energy that goes into compressing a gas is "stored" in it. This energy is called **expansion work**. The formulas for calculating ΔE and expansion work are:

$$\Delta E = q + w, \text{ where } q = \text{heat and } w = \text{expansion work, and}$$
$$w = -P \cdot \Delta V, \text{ where } P \text{ is atmospheric pressure and } \Delta V \text{ is change in volume}$$

Heat is a more useful quantity to measure. Expansion work is only a small fraction of the energy in most reactions; the value of ΔE is close to that of q . There is another way of expressing q : the **heat of reaction** or **enthalpy change**, which has the symbol ΔH . The value of ΔH is positive when the reaction absorbs heat from its surroundings (an **endothermic** reaction). ΔH is negative when the reaction emits heat (an **exothermic** reaction). The value of ΔH for a given reaction is specific to the coefficients (= number of moles) of the reactants and products in the equation.

Finding ΔH generally requires either experimentation or using the values for ΔH for related reactions. Your textbook lists **standard heats of formation (ΔH°_f)** for many substances. These values describe ΔH for the reaction in which elements react to form one mole of a compound under standard conditions. Elements are always in their most stable natural form, and standard conditions means:

- a standard temperature (usually 25°C)
- atmospheric pressure of 1 atm (or 1 bar)
- 1.000 M concentration of any solutions

The variable for any energy exchange under standard conditions has the symbol $^\circ$ ("naught"). The symbol ΔH° is used with any such reaction, while ΔH°_f is used specifically for when a compound is formed from elements in their most natural form.



SPONTANEITY

Some reactions require an external cause to occur (e.g., pressurization or continued heating); others happen naturally and continuously. Any chemical reaction or physical change that occurs without outside influences is **spontaneous**. In a **nonspontaneous** process, an outside influence must act constantly to make the process happen.

The factor that determines whether a process is spontaneous is **entropy**. Entropy is a measure of randomness or chaos. Spontaneous processes always move towards greater entropy. Some ways that a system can have increased entropy are:

- *More gas molecules.* Gases are more free to move than solids or liquids. The more gas molecules, the more randomly they will be distributed within a space.
- *Solids converted to liquids* for similar reasons.
- *More molecules of any kind.* Large numbers of molecules have greater opportunity for randomness than small numbers.
- *Dissociation of certain ions.* If a substance is made up of ions with a low charge, dissociation can increase randomness. (Ions dissolved in water get hydrated. For ions with larger charges, this can actually decrease the entropy of the system.)
- *Expansion of a gas.* If a gas has a greater volume to fill, the molecules can be arranged in more ways within the space.
- *Increase of temperature.* At higher temperatures, molecules move more, increasing randomness.

We can use entropy alone to determine spontaneity by examining the entropy change of the system *and its surroundings*. The Second Law of Thermodynamics says that spontaneous processes must increase the total entropy of a system plus surroundings.

A reaction where the entropy of the system decreases will only be spontaneous if the entropy of its surroundings increase by a greater extent. Ice freezes at low temperatures spontaneously. This happens even though the system is decreasing in entropy because heat energy from the water moves out into the surroundings, increasing the surroundings' temperature, and so increasing its entropy by a greater amount. Ice melts spontaneously at high temperatures since molecules in liquids have greater entropy than ordered molecules in ice crystals and because the decrease in entropy by the surroundings (heat is absorbed from the surroundings) is smaller in scale.

Your textbook lists **standard molar entropies (S°)** of various substances. S° represents the inherent entropy of a substance when it's not participating in a reaction. We can calculate the change in entropy for a reaction by comparing the entropy before and after:

$$\Delta S^\circ = S^\circ_{\text{prod}} - S^\circ_{\text{reac}}$$

For a process that changes volume or pressure:

$$\Delta S = n R \ln \frac{V_f}{V_i} = n R \ln \frac{P_i}{P_f}$$

where n is the number of moles of gas involved and $R = 8.3145 \text{ J/K} \cdot \text{mol}$

It's difficult in practice to track the entropy in a system's surroundings. (Or in the universe at large!) However, when a spontaneous process *decreases* entropy in the



system, entropy in the surroundings is always increased by the reaction emitting heat. This means we can determine spontaneity by measuring the heat and entropy in the system together. This final measure of energy in a reaction is called **Gibbs free energy (ΔG)**:

$$\Delta G = \Delta H - T\Delta S, \text{ where } T \text{ is temperature in K}$$

If ΔG is negative, the reaction is spontaneous; if ΔG is positive, it's not. If $\Delta G = 0$, the reaction is at equilibrium. For processes that might be spontaneous in either direction (e.g., melting and freezing ice), the temperature determines the sign of ΔG .

ΔH	ΔS	ΔG
+	+	spontaneous at higher temperatures
+	-	never spontaneous
-	+	always spontaneous
-	-	spontaneous at lower temperatures

A list of **standard free energies of formation (ΔG°_f)** is in the back of your textbook. They're used just like standard heats of formation to determine the ΔG° for any reaction. ΔG° can then be used to calculate free energy for the reaction under any conditions:

$$\Delta G^\circ = \Delta G^\circ_{f, \text{prod}} - \Delta G^\circ_{f, \text{react}}$$

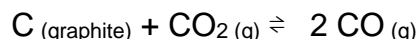
$$\Delta G = \Delta G^\circ + R T \ln Q, \text{ where } Q \text{ is the reaction quotient}$$

$\Delta G = 0$ at equilibrium, and of course $Q = K$ at equilibrium. We can rearrange the equation above to find out about K for a reaction:

$$\Delta G^\circ = -R T \ln K$$

This is useful because it is frequently difficult to determine K directly from concentrations and pressures. We can also use K to gauge the spontaneity of a reaction: if $K = 1$, the reaction is in equilibrium. If $K < 1$, the forward reaction is nonspontaneous, and if $K > 1$, the forward reaction is spontaneous.

Example 1: Determine the equilibrium constant, K_p , for the following reaction at 25°C :



Solution: First we need to know ΔG° for this reaction, and we can calculate that from the standard free energies of formation of the species in the reaction.

$$\Delta G^\circ_f(\text{C}_{(\text{graphite})}) = 0, \Delta G^\circ_f(\text{CO}_2(\text{g})) = -394.4, \Delta G^\circ_f(\text{CO}(\text{g})) = -137.2$$

$$\Delta G^\circ = \Delta G^\circ_{f, \text{prod}} - \Delta G^\circ_{f, \text{react}}$$

$$= [2 \cdot (-137.2 \text{ kJ/mol})] - [0 + (-394.4 \text{ kJ/mol})]$$

$$= 120 \text{ kJ/mol}$$

$$\Delta G^\circ = -R T \ln K$$

$$1.20 \times 10^5 \text{ J/mol} = -(8.314 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \cdot \ln K$$

$$-48.43452\dots = \ln K$$

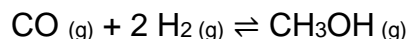
$$K = e^{-48.43452\dots} = 9.22905\dots \times 10^{-22}$$

In fact, this reaction only occurs spontaneously at high temperatures, so finding a value for K at 25°C experimentally is impossible. This answer tells us that this "equilibrium" greatly favours the reactants, underscoring that no reaction occurs at 25°C .

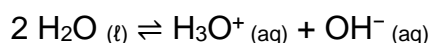


EXERCISES

- Given the following information about a reaction, what conclusions can you draw?
 - ΔH is negative
 - ΔS is negative, and the reaction is spontaneous
 - ΔG is negative
 - ΔH is positive, ΔS is positive and T is low
 - $K = 1$
- Calculate the equilibrium constant for the synthesis of methanol, as shown below, at 25°C .



- At 60°C , the dissociation constant for water, K_w , is 12.6×10^{-14} . Calculate ΔG for the reaction:



- Use the Appendix of your textbook to calculate ΔH° and ΔS° for each of the following reactions, and then calculate ΔG° at 25°C . Predict whether the reaction is spontaneous under standard-state conditions.
 - $\text{S (s, rhombic)} + \text{O}_2 \text{(g)} \rightarrow \text{SO}_2 \text{(g)}$
 - $\text{C}_2\text{H}_5\text{OH (l)} + \text{O}_2 \text{(g)} \rightarrow \text{CH}_3\text{CO}_2\text{H (l)} + \text{H}_2\text{O (l)}$
 - $\text{BaCl}_2 \text{(s)} + \text{H}_2\text{O (l)} \rightarrow \text{Ba}^{2+} \text{(aq)} + 2 \text{Cl}^- \text{(aq)} + \text{H}_2\text{O (l)}$
 - $\text{N}_2 \text{(g)} + 2 \text{H}_2 \text{(g)} \rightarrow \text{N}_2\text{H}_4 \text{(l)}$

SOLUTIONS

- The reaction is exothermic.
 - The reaction emits sufficient heat to the surroundings to make up for the decrease in entropy of the system (negative ΔS).
 - The reaction is spontaneous.
 - ΔG is positive, and the reaction is nonspontaneous.
 - The reaction is at equilibrium, and $\Delta G = 0$.
- $\Delta G^\circ = \Delta G^\circ_f \text{(products)} - \Delta G^\circ_f \text{(reactants)}$
 $= (1)(-161.9 \text{ kJ/mol}) - [(1)(-137.2 \text{ kJ/mol}) + (2)(0 \text{ kJ/mol})] = -24.7 \text{ kJ/mol}$
Now solve for K :

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-24.7 \times 10^3 \frac{\text{J}}{\text{mol}})}{\left(8.314 \frac{\text{J}}{\text{K}\cdot\text{mol}}\right)(298\text{K})} = 9.97$$
$$K = e^{9.97} = 2.1 \times 10^4$$

- $\Delta G = -RT \ln K = -(8.314 \text{ J/K}\cdot\text{mol})(333 \text{ K}) \ln (12.6 \times 10^{-14}) = 82233 \text{ J/mol}$
 $\Delta G = 82.2 \text{ kJ/mol}$
- $\Delta H^\circ = -296.8 \text{ kJ/mol}$, $\Delta S^\circ = 11.3 \text{ J/K}\cdot\text{mol}$, $\Delta G^\circ = -300.2 \text{ kJ/mol}$, spontaneous
 - $\Delta H^\circ = -492.6 \text{ kJ/mol}$, $\Delta S^\circ = -136.1 \text{ J/K}\cdot\text{mol}$, $\Delta G^\circ = -452.0 \text{ kJ/mol}$, spontaneous
 - $\Delta H^\circ = -17 \text{ kJ/mol}$, $\Delta S^\circ = -57.6 \text{ J/K}\cdot\text{mol}$, $\Delta G^\circ = -17.1 \text{ kJ/mol}$, spontaneous
 - $\Delta H^\circ = 50.6 \text{ kJ/mol}$, $\Delta S^\circ = -331.5 \text{ J/mol}$, $\Delta G^\circ = 149.4 \text{ kJ/mol}$, nonspontaneous

