# THERMODYNAMICS

Entropy

One of the most important things to remember about thermodynamics is that low-energy states are more stable than high-energy states. That's such a fundamental principle that we'll ask you to repeat it. Fill in the blank lines:

_____ energy states are more stable than_____ energy states.

Fundamentally, the universe prefers low-energy states, and also fundamentally, it tends toward disorder. When we talk about disorder, we use the term **entropy**, which is symbolized by *S*. Everything tends toward maximum entropy. When we talk about a chemical reaction and the difference between entropy of the products and entropy of the reactants, we use the symbol ΔS. If ΔS is negative, the reaction has lost entropy; the products are more "orderly" than the reactants. If ΔS is positive, the reaction has gained entropy; the products are less "orderly" than the reactants.

The State of Things

Entropy is a measure of randomness, or disorder. To get an idea of what this means, consider the two boxes below. Which one has greater entropy, or disorder? It's the one on the right.
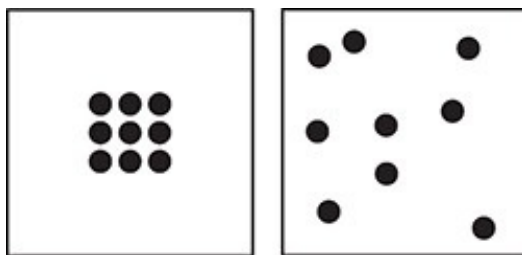
The universe, it turns out, likes disorder. Systems move toward increasing disorder. They also tend to move toward states of lower energy. For the SAT Chemistry Subject Test, when you see the word *entropy*, think "disorder," and realize that, because the universe is lazy, it tends toward maximum entropy. All things in the universe are more stable when they're in (1) states of low energy and (2) states of high entropy.

Higher Entropy + Lower Energy → More Stability

Lower Entropy + Higher Energy → Less Stability

Enthalpy

Because the universe tends toward lower energy, chemical reactions that release energy—reactions that set energy free—are favored in the universe. When we talk about the energy states of reactants or products, we use the term **enthalpy,** which is symbolized by H. High enthalpy means high-energy state, and low enthalpy means low-energy state. So, the universe likes reactions in which the enthalpy decreases—reactions in which ΔH (the change in enthalpy that occurs in the course of a reaction) is negative. These reactions are said to be **exothermic,** and they result in the release of energy in the form of heat. If, however, the enthalpy of the products is greater than the enthalpy of the reactants, then ΔH is positive and the reaction is said to be **endothermic.** Endothermic reactions require the input of energy in order to take place.

Energetic Bonds

When we say that the products are at a higher or lower energy than the reactants, we mean the bonds in the products are at a higher or lower energy. If energy is released in a reaction, that energy comes from the potential energy stored in the bonds of the reactants. If the bonds of the products have more potential energy than the bonds of the reactants, we have to supply the difference, and energy is absorbed in the reaction.

Exothermic reaction → energy is released → $\Delta H < 0$ → enthalpy decreases

Endothermic reaction → energy is absorbed → $\Delta H > 0$ → enthalpy increases

Heat of Formation

Another term you should be familiar with for the test is **heat of formation**—that is, the amount of heat that's released or absorbed when 1 mole of a compound is formed from its elements. When we talk about heat of formation, we use the same symbol we use for enthalpy change but we put a subscript "f" on it: ΔH_f. Let's consider the heat of formation of gaseous carbon dioxide, CO_2.

$$C(s) + O_2(g) \rightarrow CO_2(g); \Delta H_f = -393 \text{ kJ/mol}$$
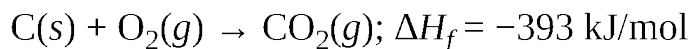
The fact that the heat of formation is negative means that heat is released during this reaction; this is an exothermic reaction. When 1 mole of CO_2 (g) is formed from its elements ($C(s)$ and $O_2(g)$), 393 kJ of energy are released.

C, Ni, Cl_2, O_2, H_2, and N_2—or all other elemental atoms or molecules—have a heat of formation of zero. Remember this for the exam.

For all elements, the heat of formation is zero.

For this test, you'll also need to keep in mind that for any reaction, the heats of formation of all the products minus the heats of formation of all the reactants is equal to ΔH_f *for the whole reaction*. The test writers might show you a reaction and give you heats of formation for all of the reactants and products. Then they'll ask you to figure out ΔH_f for the whole reaction.

That's simple to do; you just add up the heats of formation for all of the products and then all of the reactants, multiplying each by its coefficient from the balanced equation, and you've got ΔH_f for the reaction. Remember: ΔH_f (reaction) = ΔH_f (products) − ΔH_f (reactants) and the heats of formation of all elements are zero. Look at this reaction:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$
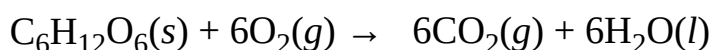
Suppose you're told that the heat of formation for

- $C_6H_{12}O_6(s)$ is −1,273 kJ/mol
- $H_2O(l)$ is −286 kJ/mol
- $CO_2(g)$ is −393 kJ/mol

(ΔH_f for $O_2(g)$, of course, is 0.)

ΔH_f for the whole reaction is equal to

$$\Delta H_f(\text{products}) - \Delta H_f(\text{reactants})$$

So

$$\Delta H_f(\text{products}) = 6 \text{ mol}(-393 \text{ kJ/mol}) + 6 \text{ mol}(-286 \text{ kJ/mol})$$
$$= -4{,}074 \text{ kJ}$$
$$\Delta H_f(\text{reactants}) = -1{,}273 \text{ kJ} + 0 \text{ kJ} = -1{,}273 \text{ kJ}$$

So, ΔH for the whole reaction = (− 4,074) − (−1,273) = −2,801 kJ. ΔH for the whole reaction is negative, which means the reaction is exothermic.

This principle also applies to reactions that occur in more than one step. **Hess's law** says that if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps. Overall, ΔH is independent of the number of steps or the pathway the reaction follows.