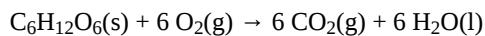


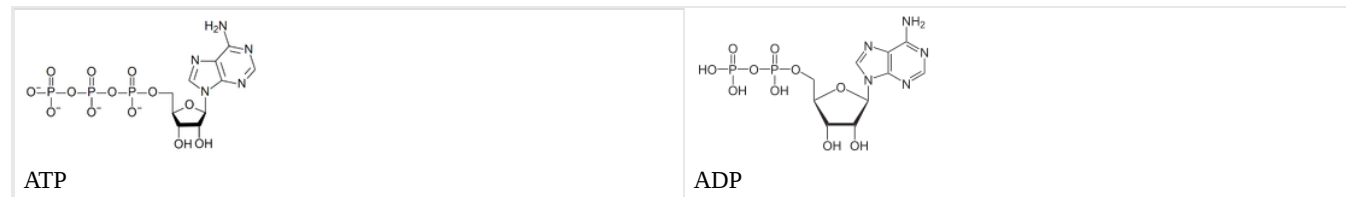
3.10.1: Biology- Muscle Energy from ATP

We have looked at sugar as a source of [Weight of Food and Energy Production | energy production] in our bodies in the last few sections, but we also know that the mechanism by which chemical energy is delivered to muscles isn't the same as the mechanism for combustion of a sugar:

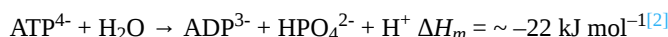


$$(25^\circ, 1 \text{ Atm}) \Delta H_m = -2808 \text{ kJ mol}^{-1} \quad (1)$$

In our bodies, adenosine Triphosphate, ATP, and adenosine diphosphate, ADP, are central intermediaries in energy delivery.



The energy of sugar metabolism is stored in the form of accumulated ATP, and when energy is needed by muscle, it is delivered by the reaction ^[1]



which is shown in an [animation here](#).

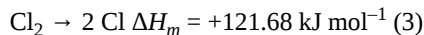
But it just doesn't make sense that this reaction should release energy, because it involves breaking a bond to remove HPO_4^{2-} , and breaking a bond should require energy. Since so many biologists misinterpret this reaction, we'll try to explain where the heat energy that drives our muscles (and growth) comes from more clearly, in terms of **standard enthalpies of formation**, below.

It's clear that there is almost an infinite number of chemical reactions whose heat energy is important to know, and chemists have measured the enthalpy changes for so many reactions that it would take several large volumes to list all the thermochemical equations. Fortunately Hess' law makes it possible to list a single value, **the standard enthalpy of formation** ΔH_f , for each compound. The standard enthalpy of formation is the enthalpy change when 1 mol of a pure substance is formed from its elements. Each element must be in the physical and chemical form which is most stable at normal atmospheric pressure and a specified temperature (usually 25°C).

For example, if we know that $\Delta H_f[\text{H}_2\text{O}(\text{l})] = -285.8 \text{ kJ mol}^{-1}$, we can immediately write the thermochemical equation

$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H_m = -285.8 \text{ kJ mol}^{-1} \quad (2)$ The elements H and O appear as diatomic molecules and in gaseous form because these are their most stable chemical and physical states. Note also that 285.8 kJ are given off *per mole* of $\text{H}_2\text{O}(\text{l})$ formed, because stronger bonds are formed (2 H-O bonds), releasing a lot of energy, while weaker bonds (O-O and H-H) are broken, requiring less energy. Equation (1) must specify formation of 1 mol $\text{H}_2\text{O}(\text{l})$, and so the coefficient of O_2 must be $\frac{1}{2}$.

The heat of formation of Cl atoms makes it clear that bond breaking is endothermic:



In some cases, such as that of water, the elements will react directly to form a compound, and measurement of the heat absorbed serves to determine ΔH_f . Quite often, however, elements do not react directly with each other to form the desired compound, and ΔH_f must be calculated by combining the enthalpy changes for other reactions. This is the case for ATP

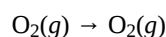
Some Standard Enthalpies of Formation at 25°C.

Some Standard Enthalpies of Formation at 25°C.

Compound	$\Delta H_f/\text{kJ mol}^{-1}$	$\Delta H_f/\text{kcal mol}^{-1}$	Compound	$\Delta H_f/\text{kJ mol}^{-1}$	$\Delta H_f/\text{kcal mol}^{-1}$
AgCl(s)	-127.068	-30.35	$\text{H}_2\text{O}(\text{g})$	-241.818	-57.79
$\text{AgN}_3(\text{s})$	+620.6	+148.3	$\text{H}_2\text{O}(\text{l})$	-285.8	-68.3
$\text{Ag}_2\text{O}(\text{s})$	-31.0	-7.41	$\text{H}_2\text{O}_2(\text{l})$	-187.78	-44.86

Compound	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$\Delta H_f^\circ/\text{kcal mol}^{-1}$	Compound	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$\Delta H_f^\circ/\text{kcal mol}^{-1}$
$\text{Al}_2\text{O}_3(\text{s})$	-1675.7	-400.40	$\text{H}_2\text{S}(\text{g})$	-20.63	-4.93
$\text{Br}_2(\text{l})$	0.0	0.00	$\text{HgO}(\text{s})$	-90.83	-21.70
$\text{Br}_2(\text{g})$	+30.907	+7.385	$\text{I}_2(\text{s})$	0.0	0.0
$\text{C}(\text{s})$, graphite	0.0	0.00	$\text{I}_2(\text{g})$	+62.438	+14.92
$\text{C}(\text{s})$, diamond	+1.895	+0.453	$\text{KCl}(\text{s})$	-436.747	-104.36
$\text{CH}_4(\text{g})$	-74.81	-17.88	$\text{KBr}(\text{s})$	-393.798	-94.097
$\text{CO}(\text{g})$	-110.525	-26.41	$\text{MgO}(\text{s})$	-601.7	-143.77
$\text{CO}_2(\text{g})$	-393.509	-94.05	$\text{NH}_3(\text{g})$	-46.11	-11.02
$\text{C}_2\text{H}_2(\text{g})$	+226.73	+54.18	$\text{NO}(\text{g})$	+90.25	+21.57
$\text{C}_2\text{H}_4(\text{g})$	+52.26	+12.49	$\text{NO}_2(\text{g})$	+33.18	+7.93
$\text{C}_2\text{H}_6(\text{g})$	-84.68	-20.23	$\text{N}_2\text{O}_4(\text{g})$	+9.16	+2.19
$\text{C}_6\text{H}_6(\text{l})$	+49.03	+11.72	$\text{NF}_3(\text{g})$	-124.7	-29.80
$\text{CaO}(\text{s})$	-635.09	-151.75	$\text{NaBr}(\text{s})$	-361.062	-86.28
$\text{CaCO}_3(\text{s})$	-1206.92	-288.39	$\text{NaCl}(\text{s})$	-411.153	-98.24
$\text{CuO}(\text{s})$	-157.3	-37.59	$\text{O}_3(\text{g})$	+142.7	+34.11
$\text{Fe}_2\text{O}_3(\text{s})$	-824.2	-196.9	$\text{SO}_2(\text{g})$	-296.83	-70.93
$\text{HBr}(\text{g})$	-36.4	-8.70	$\text{SO}_3(\text{g})$	-395.72	-94.56
$\text{HCl}(\text{g})$	-92.307	-22.06	$\text{ZnO}(\text{s})$	-348.28	-83.22
$\text{HI}(\text{g})$	+26.48	+6.33			

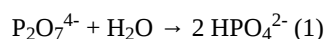
One further point arises from the definition of ΔH_f° . The standard enthalpy of formation for an element in its most stable state must be zero. If we form oxygen from its elements, for example, we are talking about the reaction



Since the oxygen is unchanged, there can be no enthalpy change, and $\Delta H_f^\circ = 0 \text{ kJ mol}^{-1}$.

Standard enthalpies of formation for some common compounds are given in the table above. These values may be used to calculate ΔH_m° for any chemical reaction so long as all the compounds involved appear in the tables. To see how and why this may be done, consider the following example.

EXAMPLE 1 Use standard enthalpies of formation below to estimate ^[3] ΔH_m° for the reaction



Note that this is like the decomposition (or "hydrolysis") of ATP to give ADP + HPO_4^{2-} , but simpler. It still **releases energy**, even though a bond is ostensibly broken between ATP and HPO_4^{2-} , **requiring energy**. What isn't seen is very important: The heats of formation of ions include "solvation energies", or in this case, energies released when water molecules bond to the HPO_4^{2-} , releasing significant amounts of energy. The energy released by "hydration" is greater than the energy required to break the P-O-P bond in ATP.

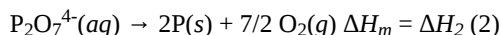
chemical species	$\Delta H_f^\circ \text{ kJ mol}^{-1}$
ATP^{4-}	-2982
$\text{H}_2\text{O} (\text{l})$	-287

ADP ³⁻	-2000
HPO ₄ ²⁻	-1299
P ₂ O ₇ ⁴⁻	-2286
H ⁺	0

Solution

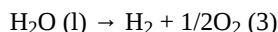
We can imagine that the reaction takes place in two steps, each of which involves only a standard enthalpy of formation. In the first step the reactants are broken into their elements, and in the second step the elements are recombined to give the products.

First, P₂O₇⁴⁻ ("pyrophosphate ion") is decomposed to its elements:



Since this is the *reverse* of formation of 1 mol P₂O₇⁴⁻ from its elements, the enthalpy change is $\Delta H_2 = \{-\Delta H_f[\text{P}_2\text{O}_7^{4-}(\text{aq})]\} = [-(-2286 \text{ kJ mol}^{-1})] = +2286 \text{ kJ mol}^{-1}$. It's positive (endothermic) because bond breaking takes energy.

Next, we break water into its elements:



Again $\Delta H_3 = -(-287) = +287 \text{ kJ mol}^{-1}$.

In the second step the elements are combined to give 2 mol HPO₄²⁻ ("inorganic monophosphate ion" or "hydrogen phosphate ion"): $2\text{P}(\text{s}) + \text{H}_2 + 2\text{O}_2(\text{g}) \rightarrow 2 \text{HPO}_4^{2-}(\text{aq}) \quad \Delta H_m = \Delta H_4 \quad (4)$ In this case $\Delta H_4 = 2 \times \Delta H_f[\text{HPO}_4^{2-}(\text{aq})] = 2 \times (-1299 \text{ kJ mol}^{-1}) = -2598 \text{ kJ mol}^{-1}$. You can easily verify that the sum of Eqs. (2) and (3) is $\text{P}_2\text{O}_7^{4-} + \text{H}_2\text{O} \rightarrow 2 \text{HPO}_4^{2-} \quad \Delta H_m = \Delta H_{\text{net}}$. Therefore $\Delta H_{\text{net}} = \Delta H_2 + \Delta H_3 + \Delta H_4 = 287 \text{ kJ mol}^{-1} + 2286 \text{ kJ mol}^{-1} - 2598 \text{ kJ mol}^{-1} = -25 \text{ kJ mol}^{-1}$. Note carefully how Example 2 was solved. In step 1 the *reactant* compound P₂O₇⁴⁻ (aq) was hypothetically decomposed to its elements. This equation was the reverse of formation of the compound, and so ΔH_2 was opposite in sign from ΔH_f . In step 2 we had the hypothetical decomposition of the other reactant, water, again ΔH_3 was opposite in sign from ΔH_f . Finally, 2 moles of the *product* HPO₄²⁻ (aq) were formed from its elements. Since 2 mol were obtained, the enthalpy change was doubled but its sign remained the same.

Any chemical reaction can be approached similarly. To calculate ΔH_m we *add* all the ΔH_f values for the products, multiplying each by the appropriate coefficient, as in step 2 above. Since the signs of ΔH_f for the reactants had to be reversed in step 1, we *subtract* them, again multiplying by appropriate coefficients. This can be summarized by the equation

$\Delta H_m = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}) \quad (4)$ The symbol Σ means "the sum of." Since ΔH_f values are given *per mole* of compound, you must be sure to multiply each ΔH_f by an appropriate coefficient derived from the equation for which ΔH_m is being calculated.

EXAMPLE 2 Use the table of standard enthalpies of formation at 25°C to calculate ΔH_m for the reaction



Once more, remember that the energy released comes from the fact that bonding between water molecules and the HPO₄²⁻ that is released **releases** more energy than it **takes** to break the P-O-P bond in ATP to give ADP + HPO₄²⁻.

Solution Using Eq. (4), we have

$$\begin{aligned} \Delta H_m &= \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}) = [\Delta H_f(\text{ADP}^{3-}) + \Delta H_f(\text{HPO}_4^{2-})] - [\Delta H_f(\text{H}_2\text{O}) + \Delta H_f(\text{ATP}^{4-})] \\ &= (-2000) \text{ kJ mol}^{-1} + (-1299) \text{ kJ mol}^{-1} - (-2982 \text{ kJ mol}^{-1}) - (-287 \text{ kJ mol}^{-1}) = -30 \text{ kJ mol}^{-1} \end{aligned}$$

Note that we were careful to use $\Delta H_f[\text{H}_2\text{O}(\text{l})]$ not $\Delta H_f[\text{H}_2\text{O}(\text{g})]$.

Even though water vapor is not the most stable form of water at 25°C, we can still use its ΔH_f value to do an interesting calculation: Find the heat energy required to vaporize 1 mole of water (we know that should be positive. It takes energy to boil water because we're breaking bonds of attraction between water molecules. $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H_f = ?$

$$\begin{aligned} \Delta H_m &= \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}) \\ &= -241.8 - (-285.8) = -241.8 + 285.8 = +44 \text{ kJ mol}^{-1} \end{aligned}$$

References

1. www.users.csbsju.edu/~hjakubo...TP_ADPTemp.htm
2. Values for ΔH_m range from below 20kJ mol^{-1} released to over 30 because biological systems are complex, and the heat energy changes depend on the presence or absence of many other molecules and ions. The reaction occurs under a range of conditions.
3. We use the word "estimate" here because biological systems are complex, and the heat energy changes depend on the presence of many other molecules. The values given are imprecise.

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