

Measurement of Heat

A thermodynamic assessment of energy output during metabolic processes requires knowledge of ways to measure the energy transferred as heat.

- When a substance is heated, its temperature typically rises. However, for a specified energy, q , transferred by heating, the size of the resulting temperature change T , depends on the “heat capacity” of the substance.
- The **heat capacity**, C , is defined as

$$C = \frac{q}{\Delta T}$$

Energy supplied as heat

Change in temperature

Unit: J / K

- The energy absorbed or released by a system as heat:

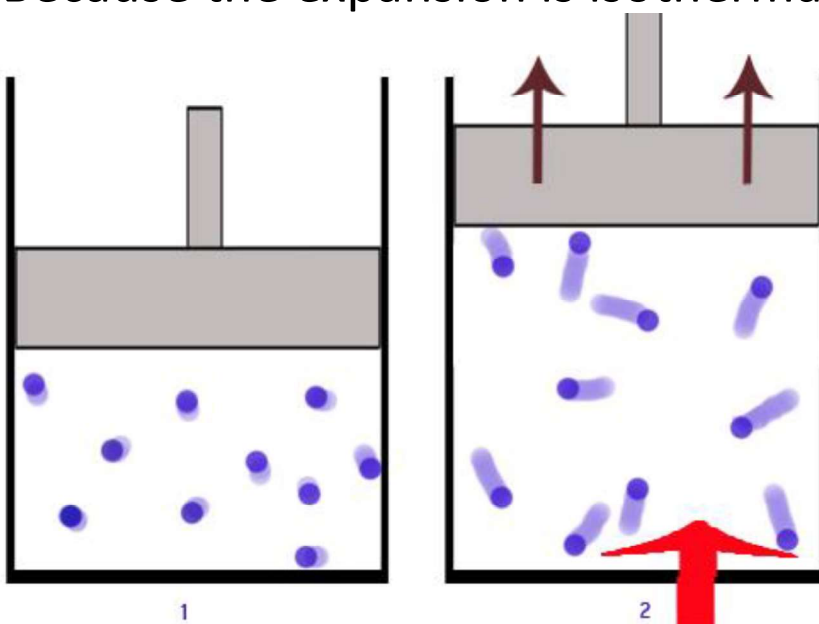
$$q = C\Delta T$$

- Heat capacity is an extensive property, a property that depends on the amount of substance in the sample.
- It is more convenient to report the heat capacity of a substance as an intensive property, a property that is independent of the amount of substance in the sample.
 - The **specific heat capacity**, C_s , the heat capacity divided by the mass of the sample $C_s = C / m$, in J / K g),
 - The **molar heat capacity**, C_m , the heat capacity divided by the amount of substance ($C_m = C / n$, in J / K mol)
- Heat capacity can change in varying volumes and pressures so we will use **heat capacity at constant pressure**, C_p *at constant pressure processes* or the **heat capacity at constant volume**, C_v *at constant volume processes*.

- Suppose that a perfect gas is undergoing an isothermal expansion. Because the expansion is isothermal, the temperature is the same before and after the expansion.

- Therefore, the internal energy is the same before and after the expansion. But for a perfect gas, the internal energy is a function of temperature only. Therefore, we can conclude that the internal energy is the same before and after the expansion.

- Energy has been added to the system as heat.



the gas is expanding, it does work on the surroundings. This work is done at the expense of the heat added to the system. We have to add heat to the system to keep the temperature constant.

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For the isothermal expansion of a perfect gas: $q = -w$

$$q = nRT \ln \frac{V_f}{V_i}$$

- When $V_f > V_i$, as in an expansion, the logarithm is positive and we conclude that $q > 0$, as expected: energy flows as heat into the system to make up for the energy lost as work.
- Heat and work are *equivalent* ways of transferring energy into or out of a system in the sense that once the energy is inside, it is stored simply as “energy”: regardless of how the energy was supplied, as work or as heat, it can be released in either form.

Internal Energy

- *To understand how biological processes can store and release energy, we need to describe a very important law that relates work and heat to changes in the energy of all the constituents of a system.*
- We need some way of keeping track of the energy changes in a system. This is the job of the property called the **internal energy**, U , of the system, the sum of all the kinetic and potential contributions to the energy of all the atoms, ions, and molecules in the system.

- In practice, we do not know and cannot measure the total energy of a sample, because it includes the kinetic and potential energies of all the electrons and all the components of the atomic nuclei.
- Nevertheless, there is no problem with dealing with the *changes* in internal energy, U , because we can determine those changes by monitoring the energy supplied or lost as heat or as work. All practical applications of thermodynamics deal with ΔU , not with U itself.

$$\Delta U = w + q$$

For isothermal expansion of a perfect gas:

$$q = -W,$$

Thus,

$$\begin{aligned}\Delta U &= q + W \\ &= -W + W\end{aligned}$$

$$\Delta U = 0$$

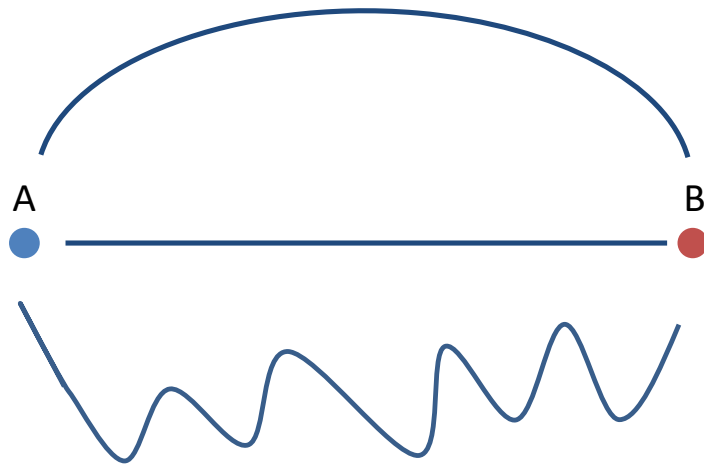
- Given the fact that our own body is a thermodynamic system, suppose you do 622 kJ of work in a spinning class and lose 82 kJ of energy as heat. What is the change in your internal energy? Disregard any matter loss by perspiration.

- To take note of the signs, we write $W = -622$ kJ (622 kJ is lost by doing work) and $q = -82$ kJ (82 kJ is lost by heating the surroundings).

$$\Delta U = w + q = (-622 \text{ kJ}) + (-82 \text{ kJ}) = -704 \text{ kJ}$$

Internal energy as a state function

- An important characteristic of the internal energy is that it is a **state function**, a physical property that depends only on the present state of the system and is independent of the path by which that state was reached.
- If we were to change the temperature of the system, then change the pressure, then adjust the temperature and pressure back to their original values, the internal energy would return to its original value too.



- The fact that U is a state function implies that *a change, ΔU , in the internal energy between two states of a system is independent of the path between them.*
- If we compress a sample of gas until it reaches a certain pressure and then cool it to a certain temperature, the change in internal energy has a particular value.
- If, on the other hand, we changed the temperature and then the pressure but ensured that the two final values were the same as in the first experiment, then the overall change in internal energy would be exactly the same as before.

Internal energy of an isolated system

- No mass or energy transfer occurs between an isolated system and the surroundings.
- An isolated system can neither do work nor heat the surroundings, it follows that its internal energy cannot change.
- Thus, the internal energy of an isolated system is constant.

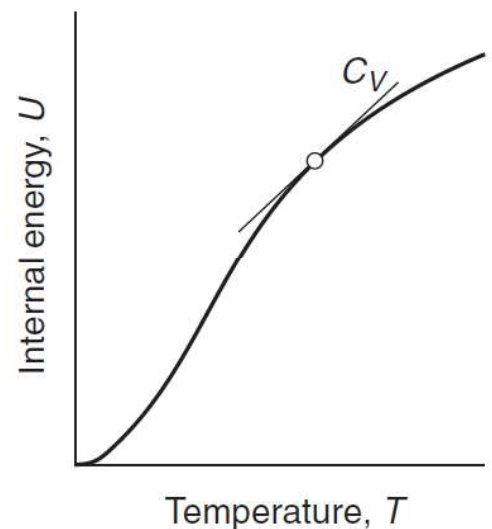
Internal energy of an isochoric system

- If we carry out a reaction in a container of constant volume, the system can do no expansion work, and provided that it can do no other kind of work (so-called non-expansion work, such as electrical work), we can set $w = 0$.

At constant volume, no non-expansion work: $\Delta U = q$

- Since $C = q / \Delta T$ and $q = \Delta U$

$$C_V = \frac{\Delta U}{\Delta T} \quad \text{or} \quad C_V = \frac{dU}{dT}$$

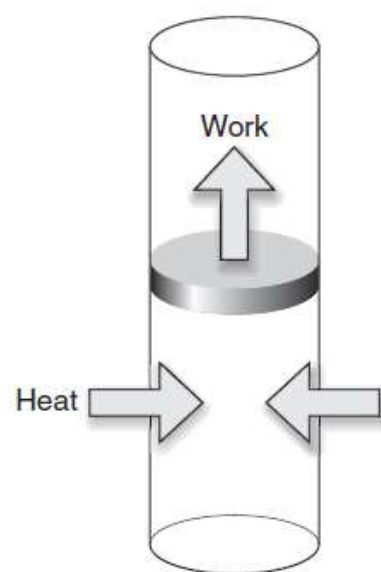


The constant volume heat capacity is the slope of a curve showing how the internal energy varies with temperature. The slope, and therefore the heat capacity, may be different at different temperatures.

The Enthalpy

Most biological processes take place in vessels that are open to the atmosphere and subjected to constant pressure and not maintained at constant volume, so we need to learn how to treat quantitatively the energy exchanges that take place by heating at constant pressure.

- When a change takes place in a system open to the atmosphere, the volume of the system changes.
- For example, the thermal decomposition of 1.0 mol $\text{CaCO}_3(\text{s})$ at 1 bar results in an increase in volume of 89 L at 800°C on account of the carbon dioxide gas produced.
- To create this large volume for the carbon dioxide to occupy, the surrounding atmosphere must be pushed back. That is, the system must perform expansion work.
- Therefore, although a certain quantity of heat may be supplied to bring about the endothermic decomposition, the increase in internal energy of the system is not equal to the energy supplied as heat because some energy has been used to do work of expansion.
- In other words, because the volume has increased, some of the heat supplied to the system has leaked back into the surroundings as work.



- Another example is the oxidation of a fat, such as tristearin, to carbon dioxide in the body. The overall reaction is



- In this exothermic reaction there is a net *decrease* in volume equivalent to the elimination of $(163 - 114)$ mol 49 mol of gas molecules for every 2 mol of tristearin molecules that reacts.
- The decrease in volume at 25°C is about 600 mL for the consumption of 1 g of fat.
- Because the volume of the system decreases, the atmosphere does work *on* the system as the reaction proceeds. That is, energy is transferred to the system as it contracts.
- For this reaction, the decrease in the internal energy of the system is less than the energy released as heat because some energy has been restored by doing work.

The Enthalpy

- We can take into account for the expansion work of the system by a new term called enthalpy (H).
- Enthalpy is a state variable that is equal to the sum of internal energy and the product of pressure and volume of the thermodynamic system.

$$H = U + pV$$

- A change in enthalpy arises from a change in the internal energy and a change in the product pV :

$$\Delta H = \Delta U + \Delta(pV)$$

At constant pressure: $\Delta H = \Delta U + p\Delta V$

Enthalpy as a state function

- Because H is defined in terms of state functions (U , p , and V), *the enthalpy is a state function.*
- The implication is that the change in enthalpy, H , when a system changes from one state to another is independent of the path between the two states.

Enthalpy change at constant pressure

- Consider a system open to the atmosphere, so that its pressure p is constant and equal to the external pressure p_{ex} .

$$\Delta H = \Delta U + p\Delta V = \Delta U + p_{\text{ex}}\Delta V$$

- The change in enthalpy of a system can be identified with the heat transferred to it at constant pressure.

$$\Delta U = w + q$$

$$w = -p_{\text{ex}}\Delta V$$

$$\Delta H = (-p_{\text{ex}}\Delta V + q) + p_{\text{ex}}\Delta V = q$$

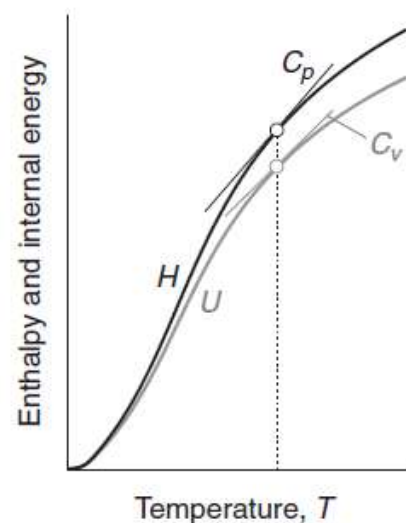
$$\Delta H = q_p$$

Enthalpy change in endothermic and exothermic processes

- An endothermic reaction ($q > 0$) taking place at constant pressure results in an increase in enthalpy ($\Delta H > 0$) because energy enters the system as heat.
- On the other hand, an exothermic process ($q < 0$) taking place at constant pressure corresponds to a decrease in enthalpy ($\Delta H < 0$) because energy leaves the system as heat.
- All combustion reactions, including the controlled combustions that contribute to respiration, are exothermic and are accompanied by a decrease in enthalpy.

The temperature variation of the enthalpy

- The internal energy of a system rises as the temperature is increased.
- The same is true of the enthalpy, which also rises when the temperature is increased.
- The constant-volume heat capacity (C_V) tells us about the temperature- dependence of the internal energy at constant volume, so the constant pressure heat capacity (C_p) tells us how the enthalpy of a system changes as its temperature is raised at constant pressure.



$$C = q/\Delta T$$

$$C_V = \frac{\Delta U}{\Delta T} \quad \text{At constant volume}$$

$$C_p = \frac{\Delta H}{\Delta T} \quad \text{at constant pressure}$$

$$C_V = \frac{dU}{dT} \quad \text{At constant volume}$$

$$C_p = \frac{dH}{dT} \quad \text{at constant pressure}$$

- When temperature of 100 g of water (5.55 mol H₂O) is raised from 20°C to 80°C at constant pressure, calculate the change in the enthalpy of the sample. ($C_{p,m} = 75.29 \text{ J/K mol}$)

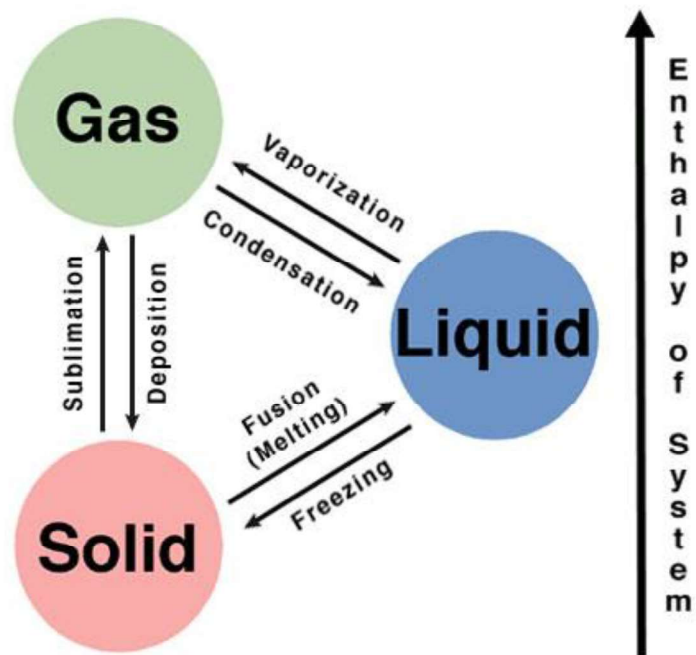
$$\Delta T = +60 \text{ K}$$

$$\Delta H = C_p \Delta T = n C_{p,m} \Delta T = (5.55 \text{ mol}) \times (75.29 \text{ J K}^{-1} \text{ mol}^{-1}) \times (60 \text{ K}) \\ = +25 \text{ kJ}$$

The greater the temperature rise, the greater the change in enthalpy and therefore the more heating required to bring it about. Note that this calculation is only approximate, because the heat capacity depends on the temperature, and we have used an average value for the temperature range of interest.

The enthalpy of physical change

- The **standard state** of a substance is the pure substance at exactly 1 bar.
- The standard molar enthalpy of a substance, is denoted as H_m^\ominus at the standard pressure of 1 bar, p^\ominus .
- **Phase** is a specific state of matter that is uniform throughout in composition and physical state.
- The conversion of one phase of a substance to another phase is called a **phase transition**.
- Phase transitions are accompanied by a change of enthalpy, for the rearrangement of atoms or molecules usually requires or releases energy.



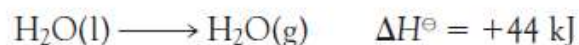
Enthalpy of vaporisation

- The vaporization of a liquid, such as the conversion of liquid water to water vapor when a pool of water evaporates at 20°C or a kettle boils at 100°C, is an endothermic process ($\Delta H > 0$), because heating is required to bring about the change.
- At a molecular level, molecules are being driven apart from the grip they exert on one another, and this process requires energy.

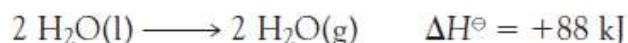
One of the body's strategies for maintaining its temperature at about 37°C is to use the endothermic character of the vaporization of water, because the evaporation of **perspiration** requires energy and withdraws it from the skin.

- The energy that must be supplied as heat at constant pressure per mole of molecules that are vaporized under standard conditions (that is, pure liquid at 1 bar changing to pure vapor at 1 bar) is called the **standard enthalpy of vaporization** of the liquid and is denoted $\Delta_{\text{vap}}H^{\ominus}$.
- For example, 44 kJ of heat is required to vaporize 1 mol $\text{H}_2\text{O}(\text{l})$ at 1 bar and 25°C , so $\Delta_{\text{vap}}H^{\ominus} = 44 \text{ kJ/mol}$.

- A thermochemical equation shows the standard enthalpy change (including the sign) that accompanies the conversion of an amount of reactant equal to its stoichiometric coefficient in the accompanying chemical equation (in this case, 1 mol H₂O).



- If the stoichiometric coefficients in the chemical equation are multiplied through by 2, then the thermochemical equation would be written

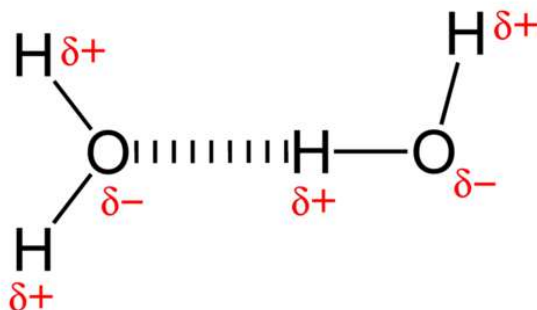


- This equation signifies that 88 kJ of heat is required to vaporize 2 mol H₂O(l) at 1 bar and at 298.15 K.

- There are some striking differences in standard enthalpies of vaporization: although the value for water is 44 kJ/mol, that for methane, CH₄, at its boiling point is only 8 kJ/mol.
- Even allowing for the fact that vaporization is taking place at different temperatures, the difference between the enthalpies of vaporization signifies that water molecules are held together in the bulk liquid much more tightly than methane molecules are in liquid methane.

What do you think is the reason for this?

- The interaction responsible for the low volatility of water is the hydrogen bond, an attractive interaction between two species that arises from a link of the form A–H ··· B, where A and B are highly electronegative elements (such as oxygen) and B possesses one or more lone pairs of electrons (such as oxygen in H₂O).



- The high enthalpy of vaporization of water has profound ecological consequences, for it is partly responsible for the survival of the oceans and the generally low humidity of the atmosphere.
- If only a small amount of heat had to be supplied to vaporize the oceans, the atmosphere would be much more heavily saturated with water vapor than is in fact the case.



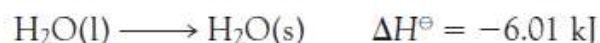
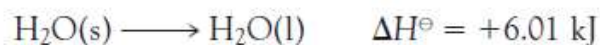
Lava meets the ocean off the coast of Hawaii. The heat from the lava converts liquid water from the ocean to clouds of steam with dramatic effect.

Enthalpy of fusion

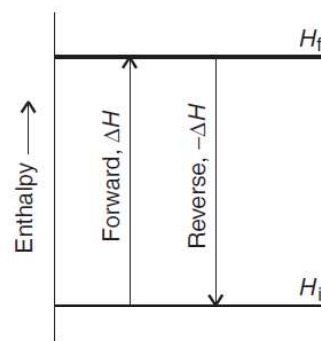
- Another common phase transition is **fusion**, or melting, as when ice melts to water. The change in molar enthalpy that accompanies fusion under standard conditions (pure solid at 1 bar changing to pure liquid at 1 bar) is called the **standard enthalpy of fusion**, $\Delta_{\text{fus}}H^\ominus$.
- Its value for water at 0°C is 6.01 kJ/mol which signifies that 6.01 kJ of energy is needed to melt 1 mol H₂O(s) at 0°C and 1 bar.
- Notice that the enthalpy of fusion of water is much less than its enthalpy of vaporization. In vaporization the molecules become completely separated from each other, whereas in melting the molecules are merely loosened without separating completely.

Enthalpies of condensation and freezing

- The reverse of vaporization is **condensation** and the reverse of fusion (melting) is **freezing**.
- The molar enthalpy changes are, respectively, the **negative of the enthalpies of vaporization and fusion**, because the energy that is supplied (during heating) to vaporize or melt the substance is released when it condenses or freezes.
- It is always the case that *the enthalpy change of a reverse transition is the negative of the enthalpy change of the forward transition* (under the same conditions of temperature and pressure):



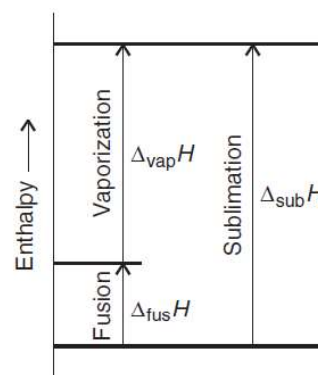
$$\Delta_{\text{forward}} H^\ominus = -\Delta_{\text{reverse}} H^\ominus$$



Enthalpy of sublimation

- The direct conversion of a solid to a vapor is called **sublimation**.
- Sublimation can be observed on a cold, frosty morning, when frost vanishes as vapor without first melting.
- The vaporization of solid carbon dioxide (“dry ice”) is another example of sublimation.
- The standard molar enthalpy change accompanying sublimation is called the **standard enthalpy of sublimation**, $\Delta_{\text{sub}}H^{\ominus}$.
- Because enthalpy is a state property, the same change in enthalpy must be obtained both in the *direct* conversion of solid to vapor and in the *indirect* conversion, in which the solid first melts to the liquid and then that liquid vaporizes. Thus,

$$\Delta_{\text{sub}}H^{\ominus} = \Delta_{\text{fus}}H^{\ominus} + \Delta_{\text{vap}}H^{\ominus}$$



- Calculate the standard enthalpy of sublimation of water at 0°C.
 - **Strategy:**the two enthalpies that are added together must be for the same temperature, so to get the enthalpy of sublimation of water at 0°C:
 - $\Delta_{\text{fus}}H^\ominus (\text{H}_2\text{O}, 273.15^\circ\text{K}) = 6.01 \text{ kJ/mol}$
 - $\Delta_{\text{vap}}H^\ominus (\text{H}_2\text{O}, 273.15^\circ\text{K}) = 45.07 \text{ kJ/mol}$

$$\begin{aligned}\Delta_{\text{sub}}H^\ominus &= \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus = 6.01 \text{ kJ mol}^{-1} + 45.07 \text{ kJ mol}^{-1} \\ &= 51.08 \text{ kJ mol}^{-1}\end{aligned}$$

- This result is an example of a more general statement:
- *The enthalpy change of an overall process is the sum of the enthalpy changes for the steps (observed or hypothetical) into which it may be divided.*

Hess's Law

The enthalpy of chemical change

To understand bioenergetics, we need to account for the flow of energy during chemical reactions as individual chemical bonds are broken and made.

- The thermochemical equation for the dissociation, or breaking, of a chemical bond can be written with the hydroxyl radical OH(g) as an example:



- The corresponding standard molar enthalpy change is called the **bond enthalpy**, so we would report the H–O bond enthalpy as 428 kJ/mol.
- All bond enthalpies are positive, so bond dissociation is an endothermic process.

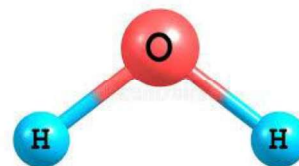
- A complication when dealing with bond enthalpies is that their values depend on the molecule in which the two linked atoms occur. For instance, the total standard enthalpy change for the atomization (the complete dissociation into atoms) of water:



- is not twice the O–H bond enthalpy in H_2O even though two O–H bonds are dissociated. There are in fact two different dissociation steps. In the first step, an O–H bond is broken in an H_2O molecule:

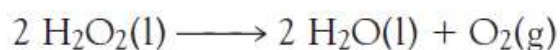


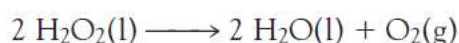
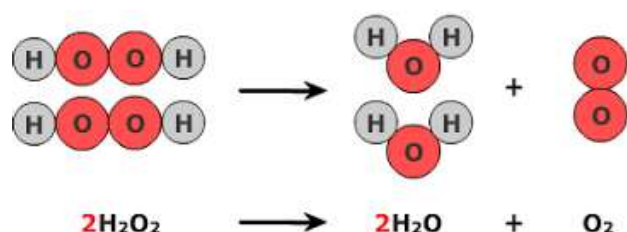
- In the second step, the O–H bond is broken in an OH radical:



- The sum of the two steps is the atomization of the molecule. As can be seen from this example, the O–H bonds in H_2O and HO have similar but not identical bond enthalpies.
- Although accurate calculations must use bond enthalpies for the molecule in question and its successive fragments, when such data are not available, there is no choice but to make estimates by using **mean bond enthalpies**, ΔH_{B} , which are the averages of bond enthalpies over a related series of compounds

- In the aqueous environment of biological cells, hydrogen peroxide—a very reactive species—is formed as a result of some processes involving O_2 . The enzyme catalase helps rid organisms of toxic hydrogen peroxide by accelerating its decomposition.
- Estimate the standard enthalpy change for the following reaction in which liquid hydrogen peroxide decomposes into O_2 and water at 25°C .





- **Strategy:** Break the overall process down into a sequence of steps such that their sum is the chemical equation required.
- Always ensure, when using bond enthalpies, that all the species are in the gas phase.

	$\Delta H^\ominus/\text{kJ}$
Vaporization of 2 mol $\text{H}_2\text{O}_2(\text{l})$, $2 \text{H}_2\text{O}_2(\text{l}) \longrightarrow 2 \text{H}_2\text{O}_2(\text{g})$	$2 \times (+51.6)$
Dissociation of 4 mol O–H bonds:	$4 \times (+463)$
Dissociation of 2 mol O–O bonds in HO–OH:	$2 \times (+213)$
Overall, so far: $2 \text{H}_2\text{O}_2(\text{l}) \longrightarrow 4 \text{H}(\text{g}) + 4 \text{O}(\text{g})$	+2381

- The standard enthalpy change for bond formation (the reverse of dissociation) is the negative of the bond enthalpy.

	$\Delta H^\ominus/\text{kJ}$
Formation of 4 mol O–H bonds:	$4 \times (-492)$
Formation of 1 mol O_2 :	-497
Overall, in this step: $4 \text{O}(\text{g}) + 4 \text{H}(\text{g}) \longrightarrow 2 \text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$	-2465

- The final stage of the reaction is the condensation of 2 mol $\text{H}_2\text{O}(\text{g})$:



- The sum of the enthalpy changes is:

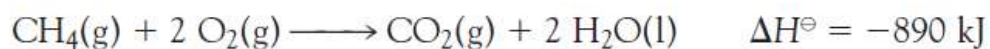
$$\Delta H^\ominus = (+2381 \text{ kJ}) + (-2465 \text{ kJ}) + (-88 \text{ kJ}) = -172 \text{ kJ}$$

The enthalpy of combustion

Photosynthesis and the oxidation of organic molecules are the most important processes that supply energy to organisms. Here, we begin a quantitative study of biological energy conversion by assessing the thermochemical properties of fuels.

- The consumption of a fuel in a furnace or an engine is the result of a combustion.
- The **standard enthalpy of combustion**, $\Delta_c H^\theta$, is the standard change in enthalpy per mole of combustible substance.

- Combustion of methane:



- $\Delta_c H^\ominus$ is a molar quantity and is obtained from the value of ΔH^\ominus by dividing by the amount of organic reactant consumed. Thus,

$$\Delta_c H^\ominus (\text{CH}_4, \text{g}) = - 890 \text{ kJ/mol}$$

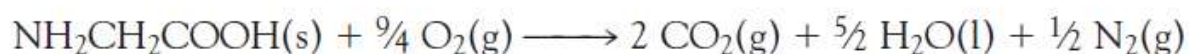
- The relation $\Delta U = q_v$, the energy transferred as heat at constant volume is equal to the change in internal energy, ΔU , not ΔH .
- To convert from ΔU to ΔH , we need to note that the molar enthalpy of a substance is related to its molar internal energy by $H_m = U_m + pV_m$.
- For condensed phases, pV_m is so small, it may be ignored.
- For example, the molar volume of liquid water is $18 \text{ cm}^3 \text{ mol}^{-1}$, and at 1.0 bar:

$$pV_m = (1.0 \times 10^5 \text{ Pa}) \times (18 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) = 1.8 \text{ Pa m}^3 \text{ mol}^{-1} \\ = 1.8 \text{ J mol}^{-1}$$

- However, the molar volume of a gas, and therefore the value of pV_m , is about 1000 times greater and cannot be ignored.
- For ideal gases we can replace pV_m with RT .
- Therefore, if in the chemical equation the difference (products - reactants) in the stoichiometric coefficients of *gas phase* species is gas, $\Delta\nu_{\text{gas}}$.

$$\Delta_c H = \Delta_c U + \Delta\nu_{\text{gas}} RT$$

- The energy released as heat by the combustion of the amino acid glycine is 969.6 kJ/mol at 298.15 K, calculate $\Delta_c H$ given that $\Delta_c U = 969.6$ kJ/mol.



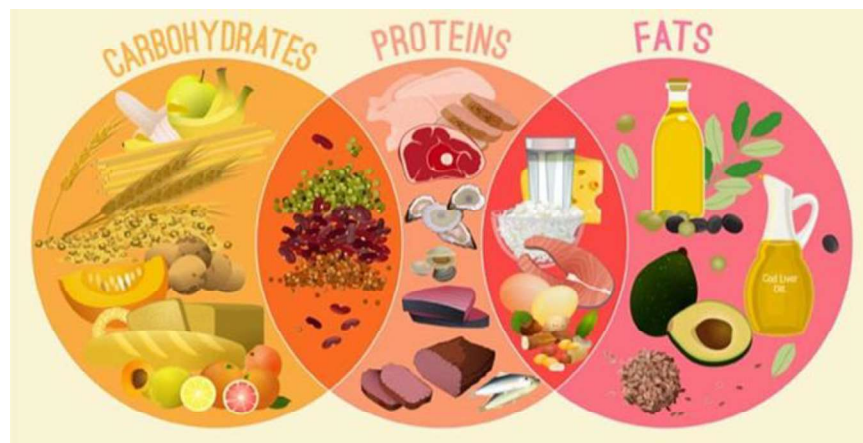
$$\Delta \nu_{\text{gas}} = (2 + \frac{1}{2}) - \frac{9}{4} = \frac{1}{4}$$

$$\begin{aligned} \Delta_c H &= \Delta_c U + \frac{1}{4}RT = -969.6 \text{ kJ mol}^{-1} + \frac{1}{4} \times (8.3145 \times 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K}) \\ &= -969.6 \text{ kJ mol}^{-1} + 0.62 \text{ kJ mol}^{-1} = -969.0 \text{ kJ mol}^{-1} \end{aligned}$$

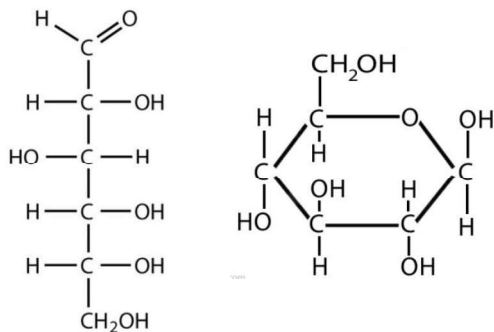
The enthalpy of biological fuels

- A typical 18- to 20-year-old man requires a daily energy input of about 12 MJ ($1 \text{ MJ} = 10^6 \text{ J}$); a woman of the same age needs about 9 MJ.
- If the entire consumption were in the form of glucose, which has a **specific enthalpy** (the enthalpy of combustion per gram of material) of 16 kJ/g, meeting energy needs would require the consumption of 750 g of glucose by a man and 560 g by a woman.

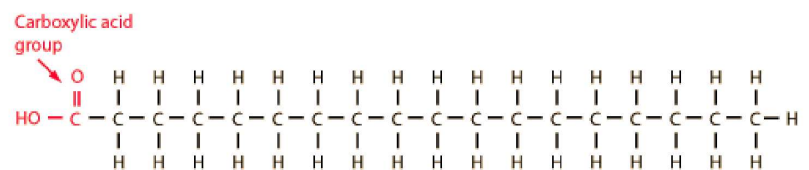
- In fact, the complex carbohydrates more commonly found in our diets have slightly higher specific enthalpies (17 kJ/g) than glucose itself, so a carbohydrate diet is slightly less daunting than a pure glucose diet, as well as being more appropriate in the form of fiber, the indigestible cellulose that helps move digestion products through the intestine.



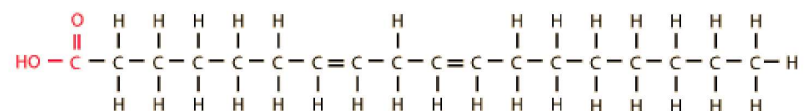
- The specific enthalpy of fats, which are long-chain esters such as tristearin, is much greater than that of carbohydrates, at around 38 kJ/g, slightly less than the value for the hydrocarbon oils used as fuel (48 kJ/g).
- The reason for this difference lies in the fact that many of the carbon atoms in carbohydrates are bonded to oxygen atoms and are already partially oxidized, whereas most of the carbon atoms in fats are bonded to hydrogen and other carbon atoms and hence have lower oxidation numbers.
- The presence of partially oxidized carbons lowers the energy output of a fuel.



Glucose



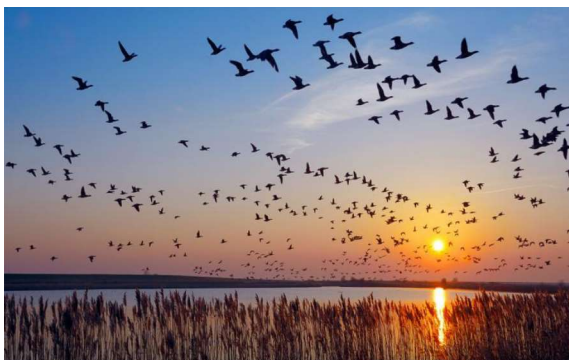
Stearic acid, an example of a saturated fatty acid



Linoleic acid, an example of an unsaturated fatty acid

Fatty Acids

- Fats are commonly used as an energy store only when the more readily accessible carbohydrates have fallen into short supply.
- Migratory birds are physiologically specialized to accumulate massive fat stores (up to 50-60% of body mass), and to transport and oxidize fats at very high rates to sustain flight for many hours or days.
- In Arctic species, the stored fat also acts as a layer of insulation; in desert species (such as the camel), the fat is also a source of water, one of its oxidation products.



- Proteins are also used as a source of energy, but their components, the amino acids, are also used to construct other proteins.
- When proteins are oxidized (to urea, $\text{CO}(\text{NH}_2)_2$), the equivalent **enthalpy density** (the enthalpy of combustion per liter of material) is comparable to that of carbohydrates.
- Not all the energy released by the oxidation of foods is used to perform work. The energy that is also released as heat needs to be discarded in order to maintain body temperature within its typical range of 35.6 to 37.8°C.
- A variety of mechanisms contribute to this aspect of **homeostasis**, the ability of an organism to counteract environmental changes with physiological responses.
- The general uniformity of temperature throughout the body is maintained largely by the flow of blood. When energy needs to be dissipated rapidly by heating, warm blood is allowed to flow through the capillaries of the skin, so producing flushing.
- Radiation is one means of heating the surroundings; another is evaporation which demands the enthalpy of vaporization of water.



Perspiration

- Calculate the energy released as heat through perspiration of 1 L of water. [$\Delta_{\text{vap}}H^\ominus = 44 \text{ kJ/mol}$], molar mass ($M = 18 \text{ g/mol}$), and mass density ($\rho = 1.0 \times 10^3 \text{ g/L}$)]

$$n = m / M$$

$$m = V \times \rho = 1 \text{ L} \times (1.0 \times 10^3 \text{ g/L}) = 1000 \text{ g}$$

$$n = 1000 \text{ g} / (18 \text{ g/mol}) = 55,56 \text{ mol}$$

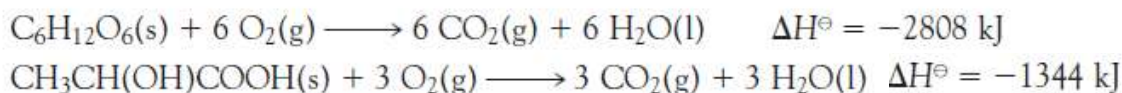
$$q = \Delta_{\text{vap}}H^\ominus \times n = 44 \text{ kJ/mol} \times 55,56 \text{ mol} = 2,44 \text{ MJ}$$

- Up to now we were dealing with simple chemical reactions that involve only 1 step. However, biochemical reactions occurring in the body are generally more complex involving several steps.
- To make progress in our study of bioenergetics, we need to develop methods for predicting the reaction enthalpies of those complex biochemical reactions.
- By combining the reaction enthalpies of known reactions we can construct the required reaction enthalpy of complex biochemical reactions.

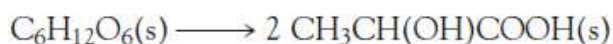
Hess's Law

- Since enthalpy is a state function, overall enthalpy change can be expressed as a sum of enthalpy changes for each step in an indirect path.
 - The individual steps need not be actual reactions that can be carried out in the laboratory—they may be entirely hypothetical reactions, the only requirement being that their equations should balance.
 - Each step must correspond to the same temperature.
- **Hess's law** states that:
 - The standard enthalpy of a reaction is the sum of the standard enthalpies of the reactions into which the overall reaction may be divided.

- In biological cells that have a plentiful supply of O_2 , glucose is oxidized completely to CO_2 and H_2O . However, when muscle cells may be deprived of O_2 during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid by the process of glycolysis. Given the thermochemical equations for the combustions of glucose and lactic acid:



- calculate the standard enthalpy for glycolysis:



	$\Delta H^\ominus/\text{kJ}$
$C_6H_{12}O_6(s) + 6 O_2(g) \longrightarrow 6 CO_2(g) + 6 H_2O(l)$	-2808
$6 CO_2(g) + 6 H_2O(l) \longrightarrow 2 CH_3CH(OH)COOH(s) + 6 O_2(g)$	$2 \times (+1344 \text{ kJ})$
Overall: $C_6H_{12}O_6(s) \longrightarrow 2 CH_3CH(OH)COOH(s)$	-120

It follows that the standard enthalpy for the conversion of glucose to lactic acid during glycolysis is 120 kJ mol^{-1} , a mere 4% of the enthalpy of combustion of glucose. Therefore, full oxidation of glucose is metabolically more useful than glycolysis, because in the former process more energy becomes available for performing work.

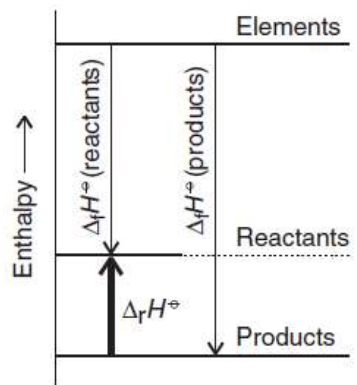
- **Self-exercise:** Calculate the standard enthalpy of the ethanol fermentation from the standard enthalpies of combustion of glucose and ethanol.

The enthalpy of formation

- The **standard reaction enthalpy**, $\Delta_r H^\ominus$, is the difference between the standard molar enthalpies of the reactants and the products, with each term weighted by the stoichiometric coefficient, ν (nu), in the chemical equation.

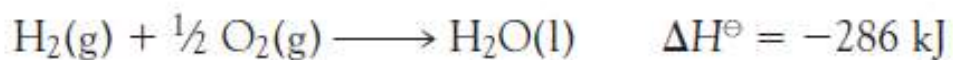
$$\Delta_r H^\ominus = \sum \nu H_m^\ominus(\text{products}) - \sum \nu H_m^\ominus(\text{reactants})$$

- The standard reaction enthalpy is the change in enthalpy of the system when the reactants in their standard states (pure, 1 bar) are completely converted into products in their standard states (pure, 1 bar), with the change expressed in kilojoules per mole of reaction.



- For calculating the reaction enthalpy, we imagine the reactants are first broken down into the elements and then the products are formed from the elements.
- Specifically, the **standard enthalpy of formation**, $\Delta_f H^\ominus$, of a substance is the standard enthalpy (per mole of the substance) for its formation from its elements in their **reference states** (the most stable form of an element under the prevailing conditions).

- Given the below equation, the standard enthalpy of formation of liquid water (at 25°C), $\Delta_f H^\ominus$ (H₂O, l), is -286 kJ/mol.



- Note that enthalpies of formation are molar quantities, so to go from ΔH^\ominus in a thermochemical equation to $\Delta_f H^\ominus$ for that substance, divide by the amount of substance formed (in this instance, by 1 mol H₂O).

- Now that we know the term standard enthalpy of formation, we can calculate the reaction enthalpy using below formula:

$$\Delta_r H^\ominus = \sum \nu \Delta_f H^\ominus(\text{products}) - \sum \nu \Delta_f H^\ominus(\text{reactants})$$

- The first term on the right is the enthalpy of formation of all the products from their elements; the second term on the right is the enthalpy of formation of all the reactants from their elements.

- Sucrose, table sugar, is a complex carbohydrate with molecular formula $C_{12}H_{22}O_{11}$ that consists of a glucose unit covalently linked to a fructose unit through a condensation reaction. Estimate the standard enthalpy of combustion of sucrose from the standard enthalpies of formation of the reactants and products.

Reaction for the combustion of sucrose:



$$\begin{aligned}\Delta_r H^\ominus &= \{12\Delta_f H^\ominus(CO_2, g) + 11\Delta_f H^\ominus(H_2O, l)\} \\ &\quad - \{\Delta_f H^\ominus(C_{12}H_{22}O_{11}, g) + 12\Delta_f H^\ominus(O_2, g)\} \\ &= \{12 \times (-393.51 \text{ kJ mol}^{-1}) + 11 \times (-285.83 \text{ kJ mol}^{-1})\} \\ &\quad - \{(-2222 \text{ kJ mol}^{-1}) + 0\} \\ &= -5644 \text{ kJ mol}^{-1}\end{aligned}$$

- **Self exercise:** Use standard enthalpies of formation to calculate the enthalpy of combustion of solid glycine to $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, and $\text{N}_2(\text{g})$.