L7

Energy in transition:

thermochemistry

Atkins&Clugston, chapter 9, p. 128-138

Thermochemistry:
phylosophical and integrative view

- Living systems are working at the same thermodynamic principles that govern machines

- In this lecture, we will explore some of the most important thermodynamic principles to understand why chemical and physical changes occur

Thermochemistry:
phylosophical and integrative view

- Thermodynamics is the study of the transformation of energy

- Thermochemistry is the branch of thermodynamics
- concerned with transformations of energy in the course of chemical reactions

Thermochemistry:
phylosophical and integrative view

Findings in biothermodynamics can be very useful in medicine and biotechnology, because all living organisms on Earth originated from the same source

Metabolism of the simplest cell has a high similarity to energy conversion that occurrs in our cells

L7 Energy in transition: thermochemistry

Thermodynamics tends to answer

how the cells (or organelles in the cell, such as mitochondria) connects the process of collection and consumption of energy

“...there is only a handful of basic concepts, and once they have been mastered much of chemistry can be explained simply...”

In the human body the power source is the chemical change of matter.

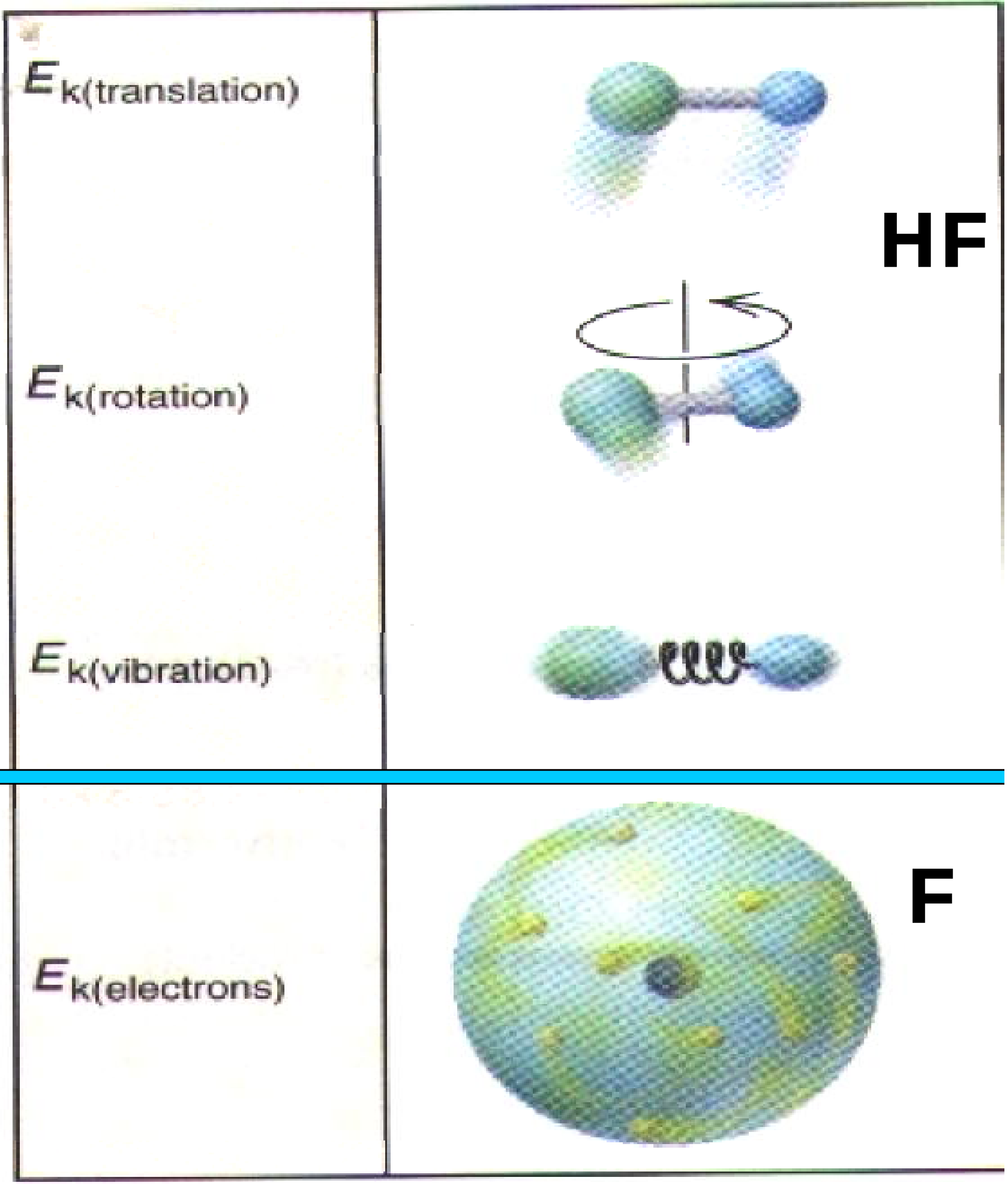
Chemical reaction is not only the change of the matter composition.

Breaking of the bonds in the **reactants and formation of new bonds in** the **products is accompanied by en**e**rgy changes.**

Contribution to kinetic energy

Example of hydrogen fluoride (HF) molecule

fluorine atom



A Contributions to kinetic energy (E_k)

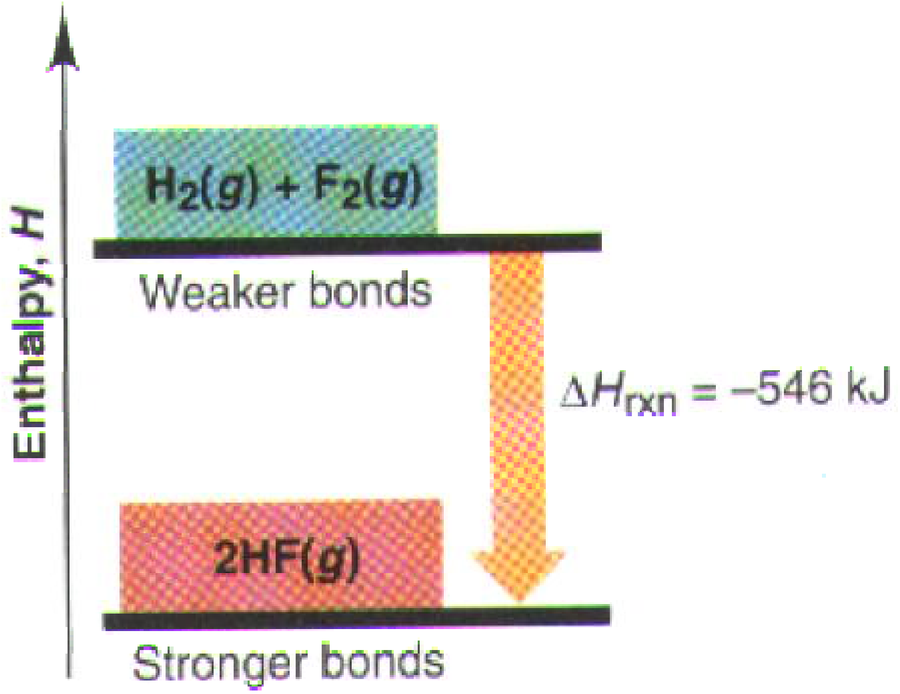
Enthalpy: heat of reaction

and the strengths of bonds

When the weaker bonds within the molecules of H_2 (H-H) and F_2 (F-F) break,

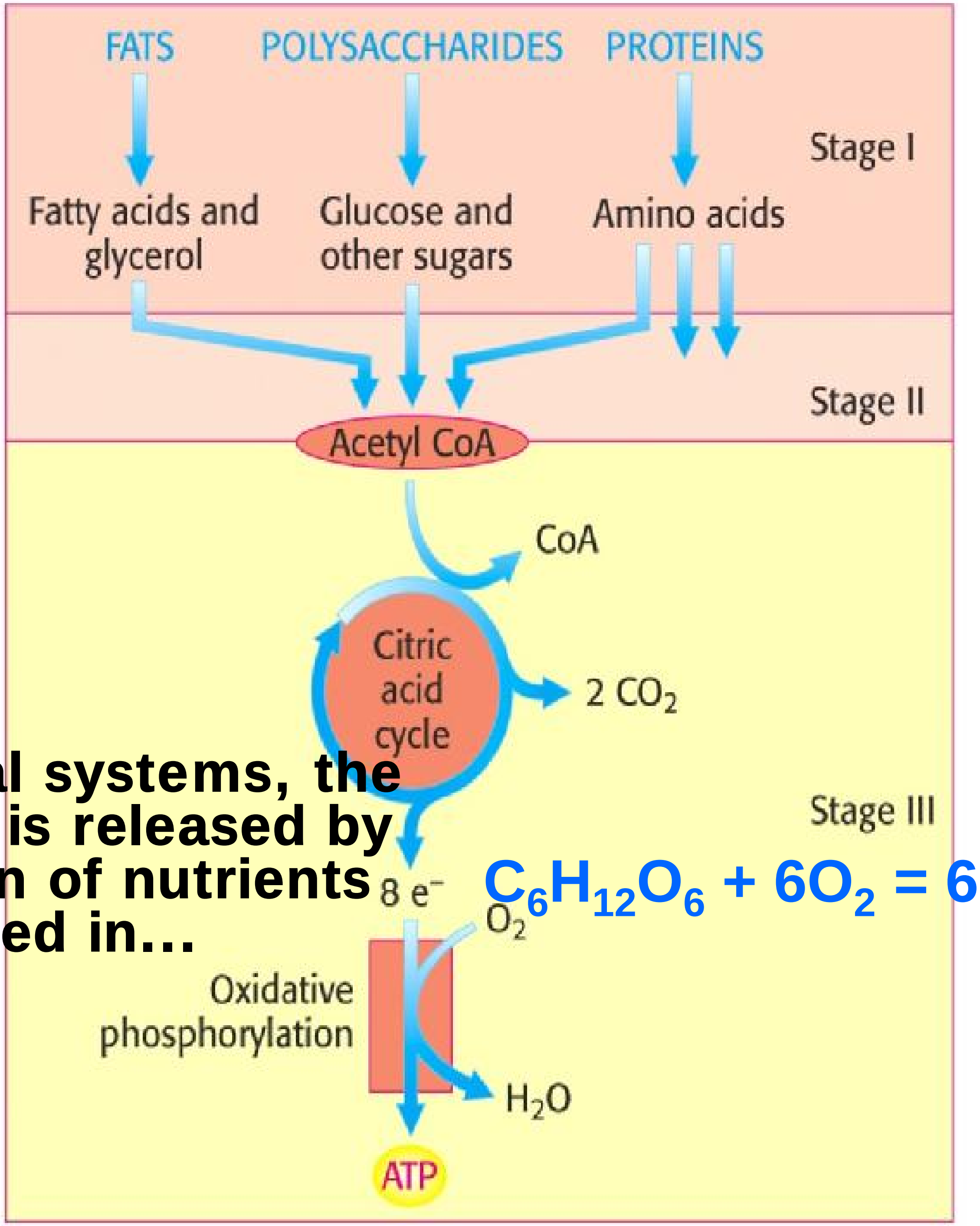
and the stronger bonds in HF form,

the difference is released as a heat of reaction.



- Understanding of energy transformation in biological systems

  is the basis for the understanding of all that happens in nature.



- in biological systems, the energy that is released by the oxidation of nutrients is transformed in…

$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$

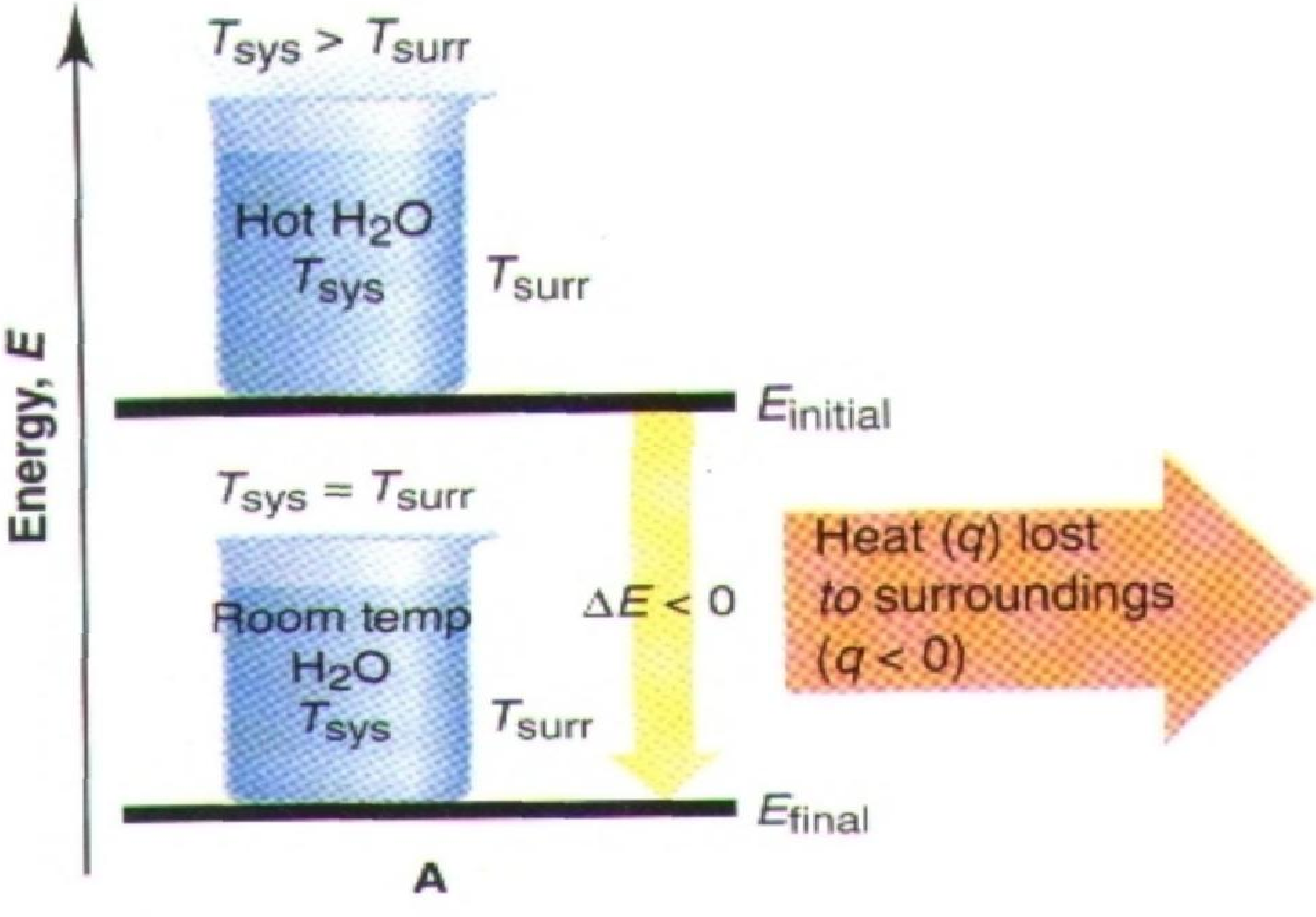
- **Nutrients are first digested in the intestines from larger molecules into smaller**

- **Further decomposition is at the cellular level to C2-degradation fragments (acetyl = CH_3COO^-)**

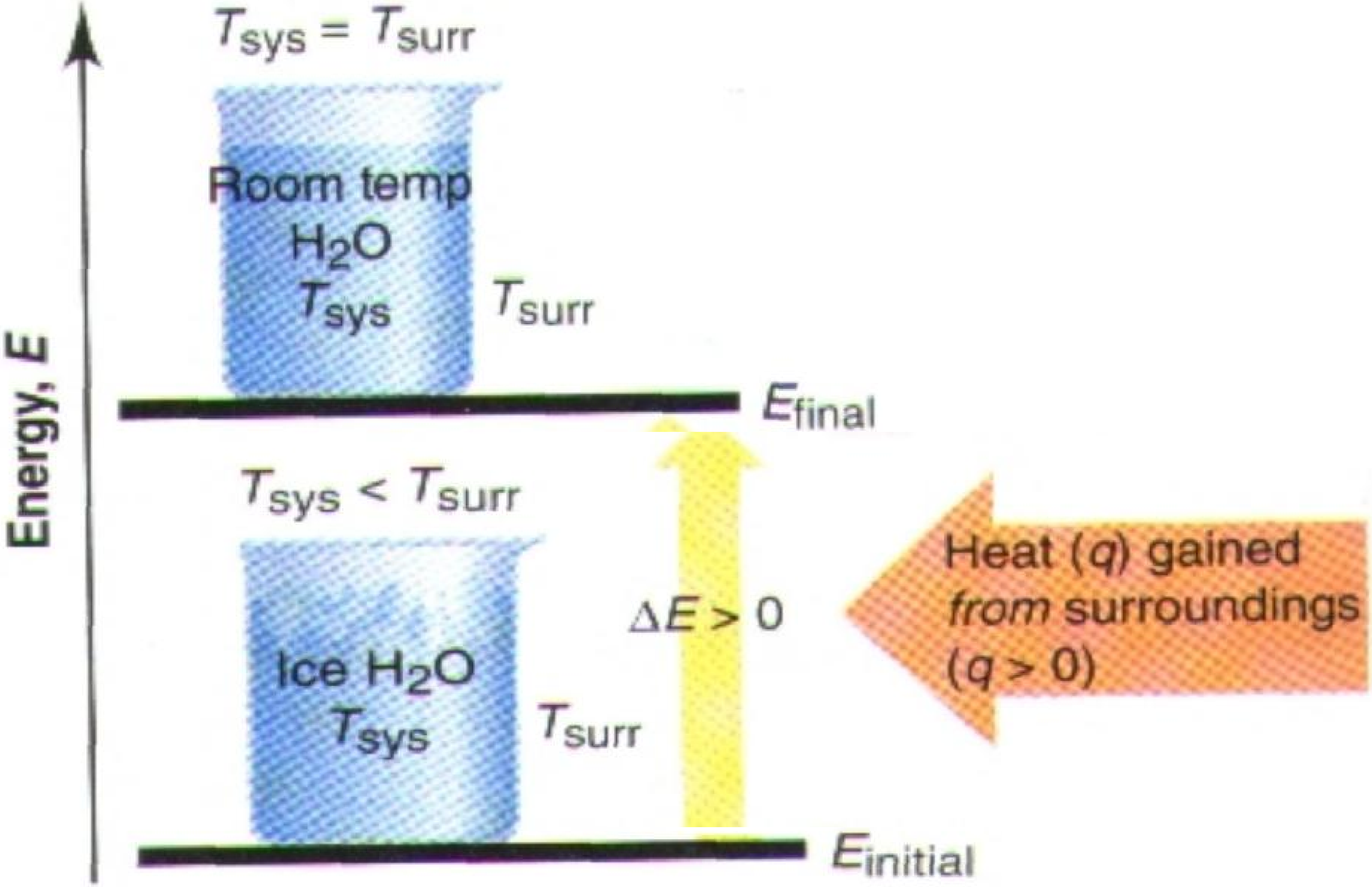
- **Acetyl fragments are ultimately oxidized to CO_2 and H_2O**

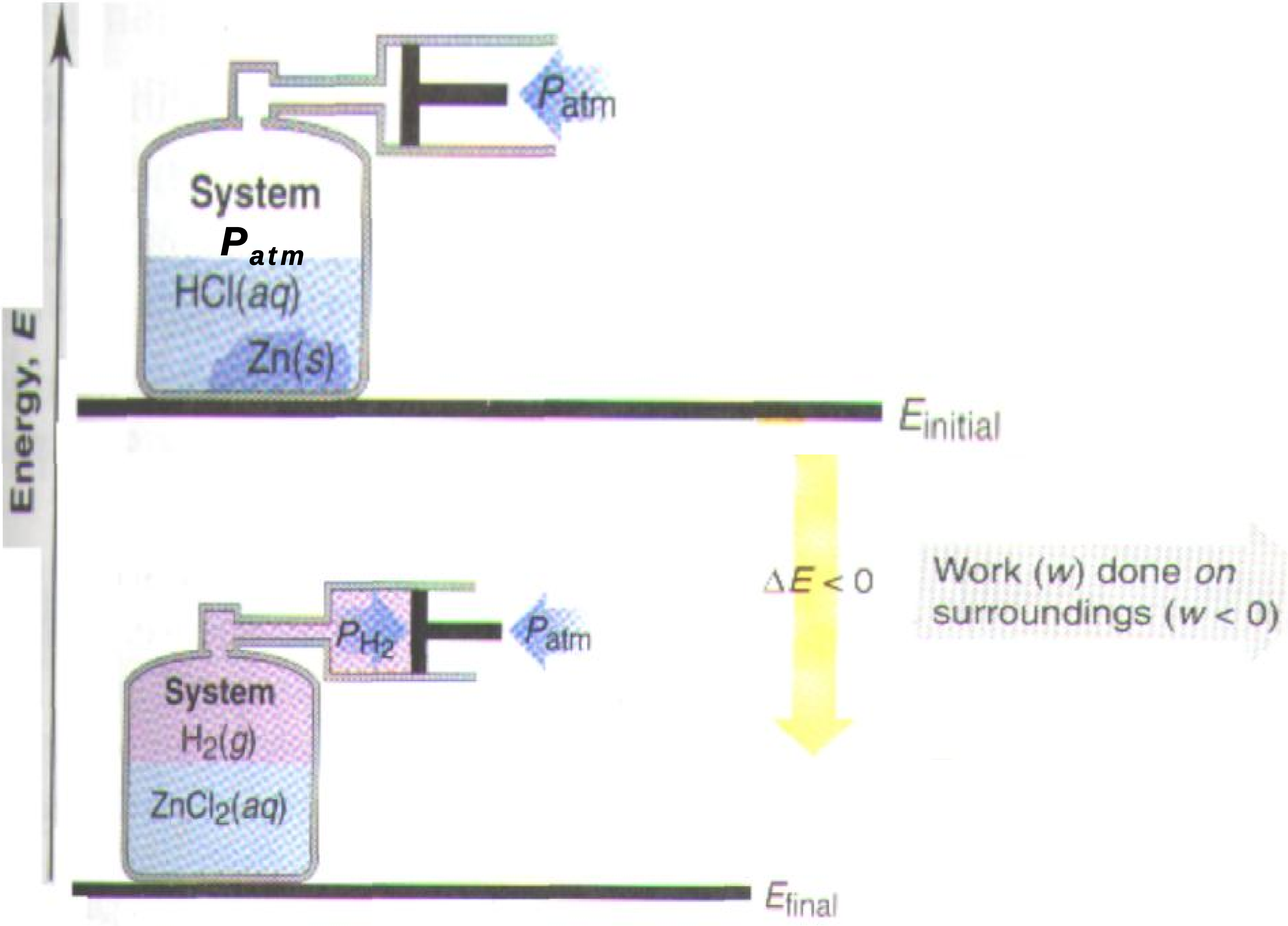
  One part of oxidation energy transits into heat and the second part is stored in the form of ATP

Figure 6.1 **A chemical system and its surroundings.** Once the contents of the flask (the orange solution) is defined as the system, the flas and the laboratory become defined as the surroundings.

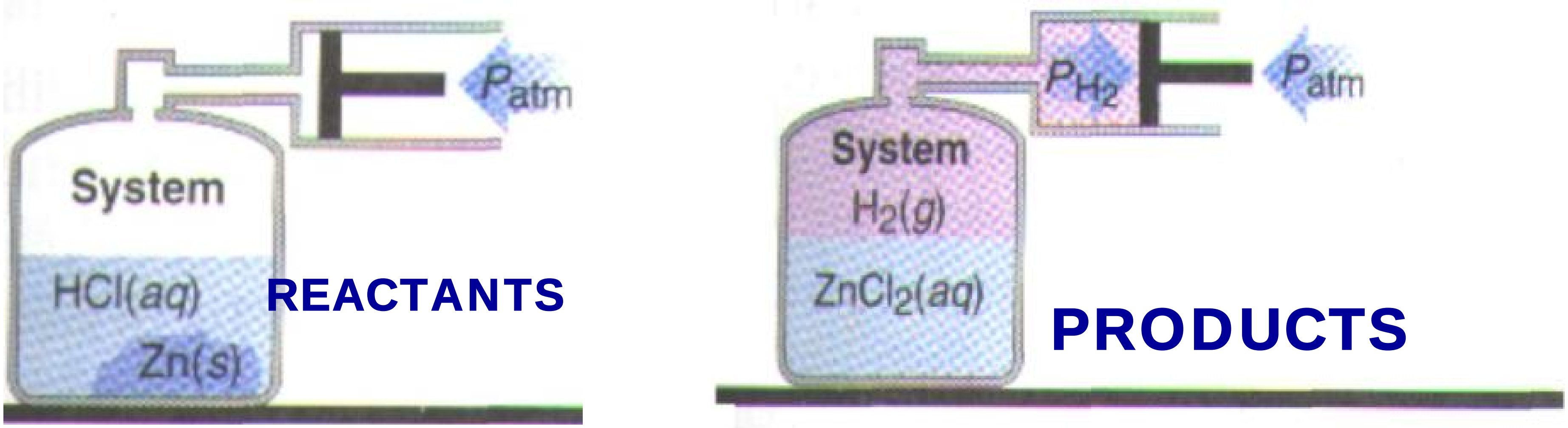


$T_{sys} > T_{surr}$
Hot H_2O
T_{sys}
T_{surr}
Energy, E
$E_{initial}$
$T_{sys} = T_{surr}$
Room temp H_2O
T_{sys}
T_{surr}
$\Delta E < 0$
Heat (q) lost *to* surroundings ($q < 0$)
E_{final}
A


Energy, E
$T_{sys} = T_{surr}$
Room temp H_2O
T_{sys}
T_{surr}
E_{final}
$T_{sys} < T_{surr}$
Ice H_2O
T_{sys}
T_{surr}
$\Delta E > 0$
Heat (q) gained *from* surroundings ($q > 0$)
$E_{initial}$


Energy, E
System
P_{atm}
$HCl(aq)$
$Zn(s)$
P_{atm}
$E_{initial}$
$\Delta E < 0$
Work (w) done *on* surroundings ($w < 0$)
System
$H_2(g)$
$ZnCl_2(aq)$
P_{H_2}
P_{atm}
E_{final}

- $Zn(s) + 2H^+(aq) + Cl^-(aq) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq) + H_2(g$



REACTANTS

PRODUCTS

- **A system losing energy as work**

- **The internal enery decreases as the reactants form products because H_2(g) does work (w) on the surrounding by pushing the piston outward.**

The development of thermodynamics

- Sadi Carnot (b. 1796, Paris)
- J.P. Joule (b. 1818, Salford)
- Lord Kelvin (b. 1824, Belfast)

- ΔU (system internal energy) = q + w

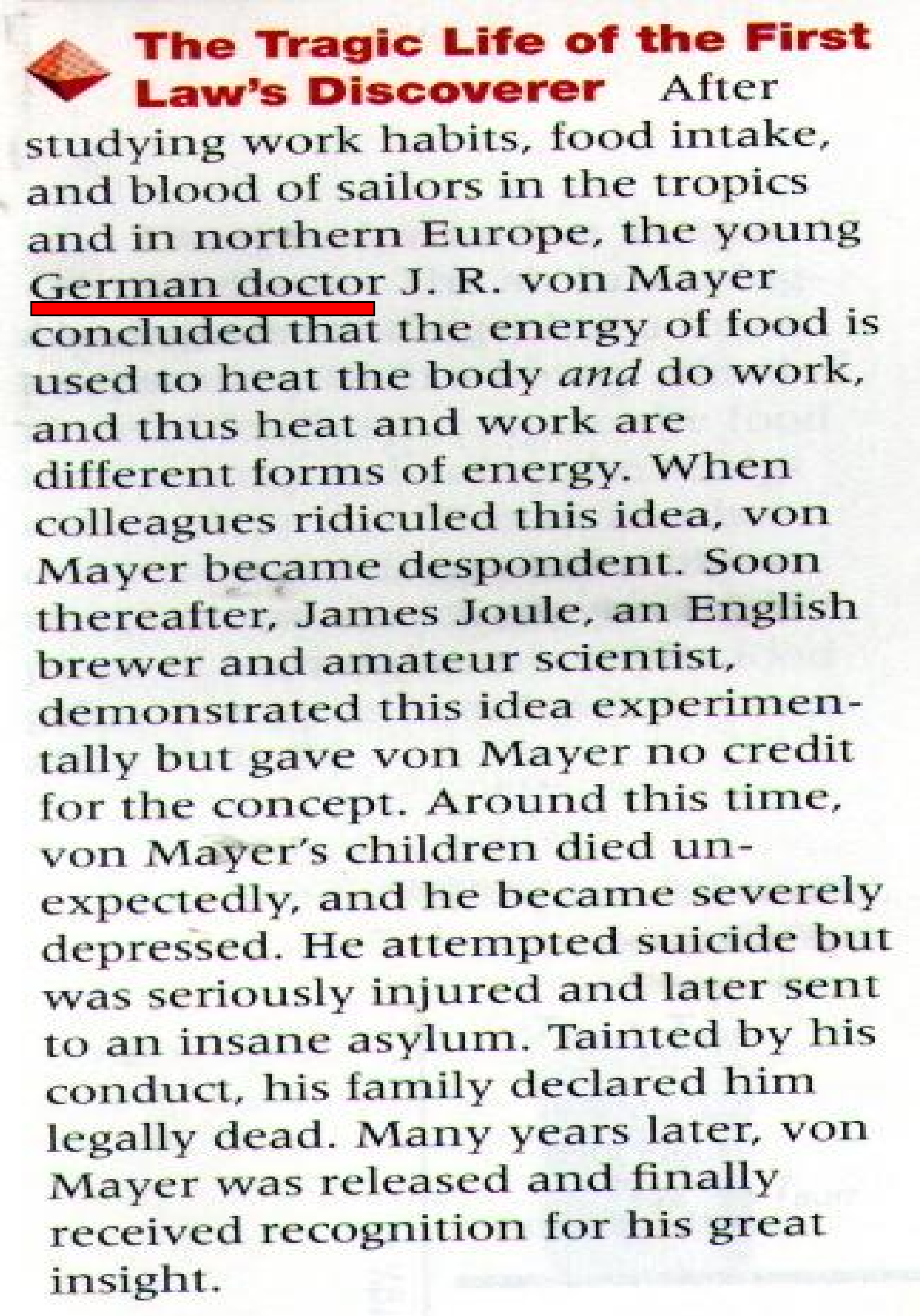
- Julius Robert Mayer (1845)

- Julius Robert Mayer

- Body can produce from the same amount of certain food more or less heat.

  He assumed that work and heat are mutually interchangeable, but that their sum must remain constant.

- $\Delta U = Q + W$



The Tragic Life of the First Law's Discoverer After studying work habits, food intake, and blood of sailors in the tropics and in northern Europe, the young German doctor J. R. von Mayer concluded that the energy of food is used to heat the body *and* do work, and thus heat and work are different forms of energy. When colleagues ridiculed this idea, von Mayer became despondent. Soon thereafter, James Joule, an English brewer and amateur scientist, demonstrated this idea experimentally but gave von Mayer no credit for the concept. Around this time, von Mayer's children died unexpectedly, and he became severely depressed. He attempted suicide but was seriously injured and later sent to an insane asylum. Tainted by his conduct, his family declared him legally dead. Many years later, von Mayer was released and finally received recognition for his great insight.

$$\Delta U = q + w$$

- The first law of thermodynamics states that energy can be neither created nor destroyed

- Energy can be transferred from one system to another as heat or as work

- If a quantity of energy, w, is transferred to a system as work

- and a quantity of energy, q, is transferred to a system as heat

- the transfer changes the internal energy U, by $DU = q + w$

- If the system did work w = -
- Because the system lost energy by doing the work (w) on the surroundings

- Work done on the system w = +

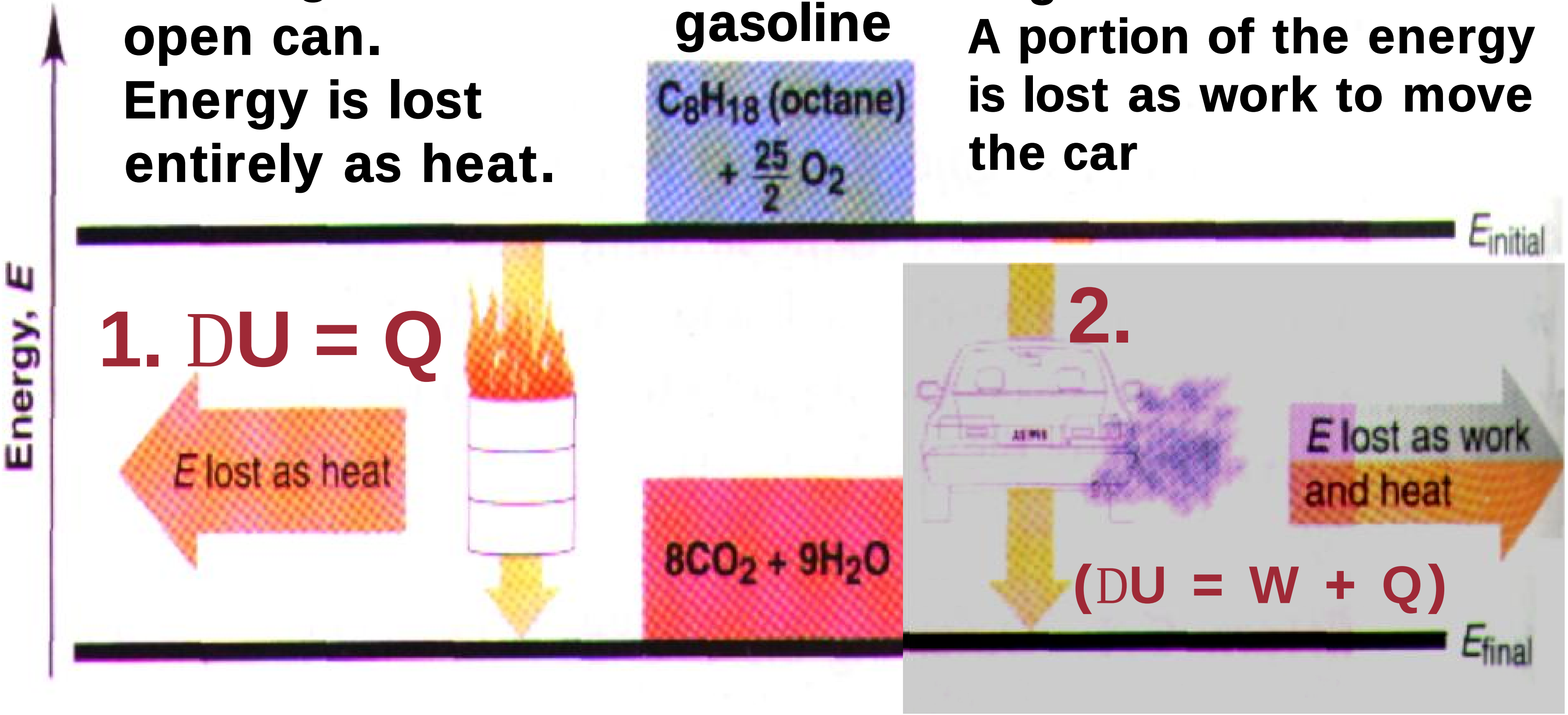
- Example
- Transfer of the heat into the surroundings 150 kJ
- Work done on the system 250 kJ

- What is the change of system internal energy?

- $\Delta U = q + w$
- $\Delta U = -150 + 250 = 100$ kJ

Two different paths for the energy change of a system

The change in internal energy when a given amount of octane burns in air is the same no metter how the energy is transferred.



Burning in an open can.
Energy is lost entirely as heat.

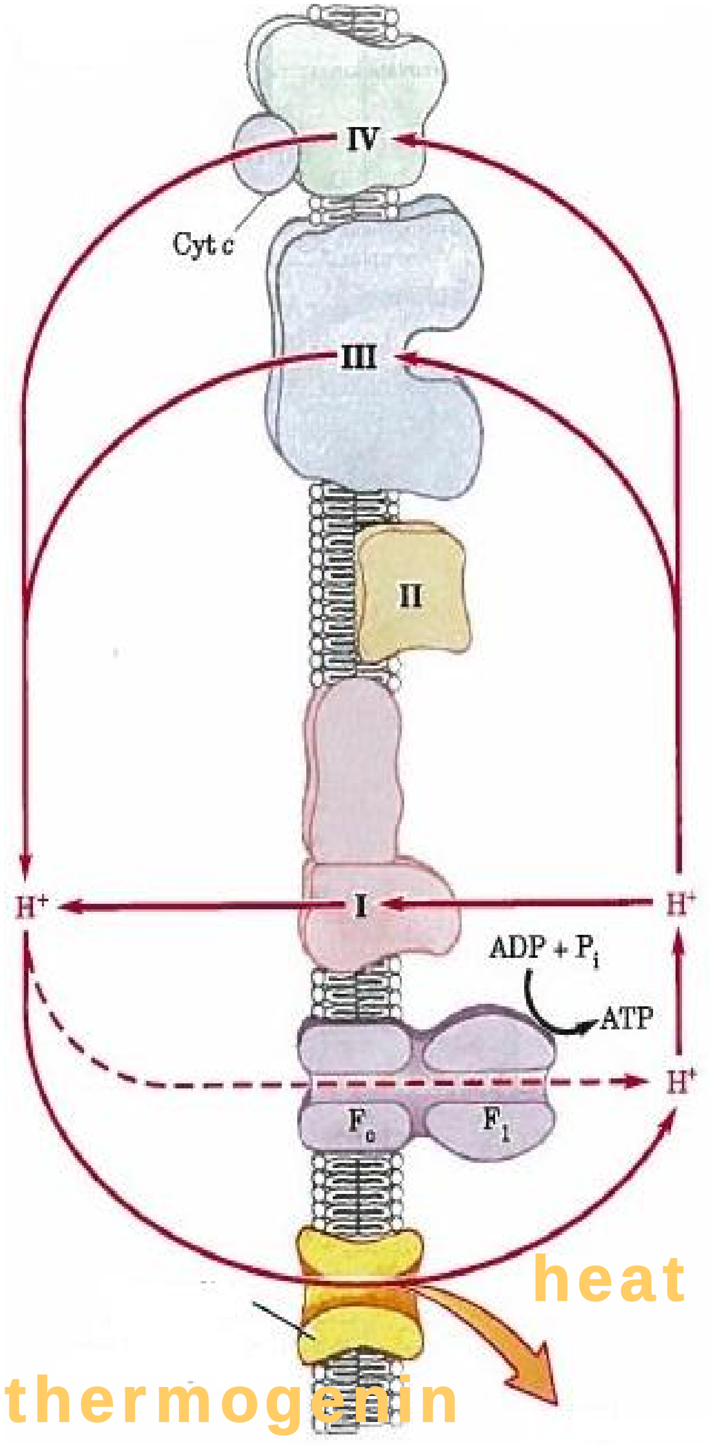
gasoline

Burning in the car engine.
A portion of the energy is lost as work to move the car

1. DU = Q

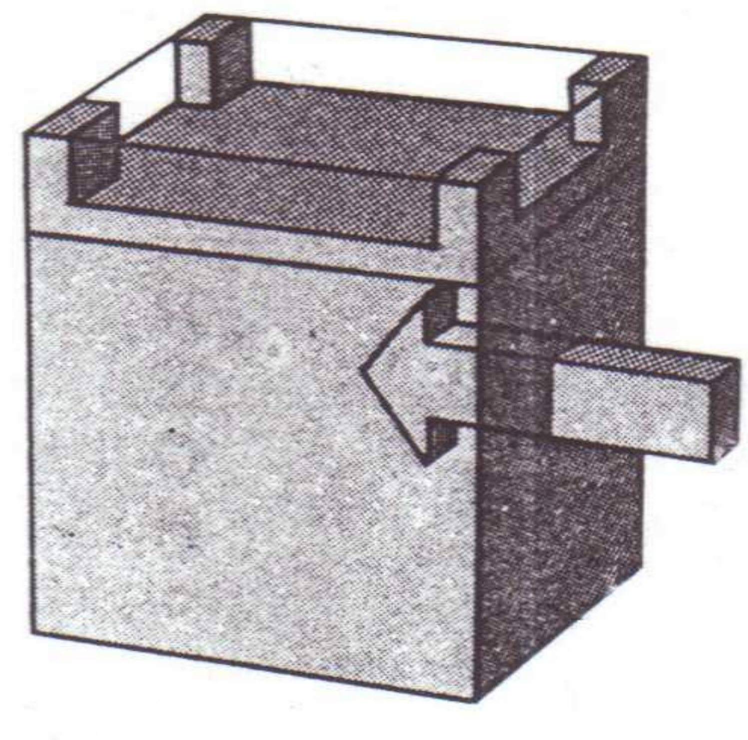
2.

(DU = W + Q)



- The current of protons move ATP synthesis throuhg the engine ATP synthase = work

- Entrance of proton in mitochondria matrix instead the movement of engine = heat



$DU = q + p\,\Delta V$

$V = \text{const}\ (\Delta V = 0)$

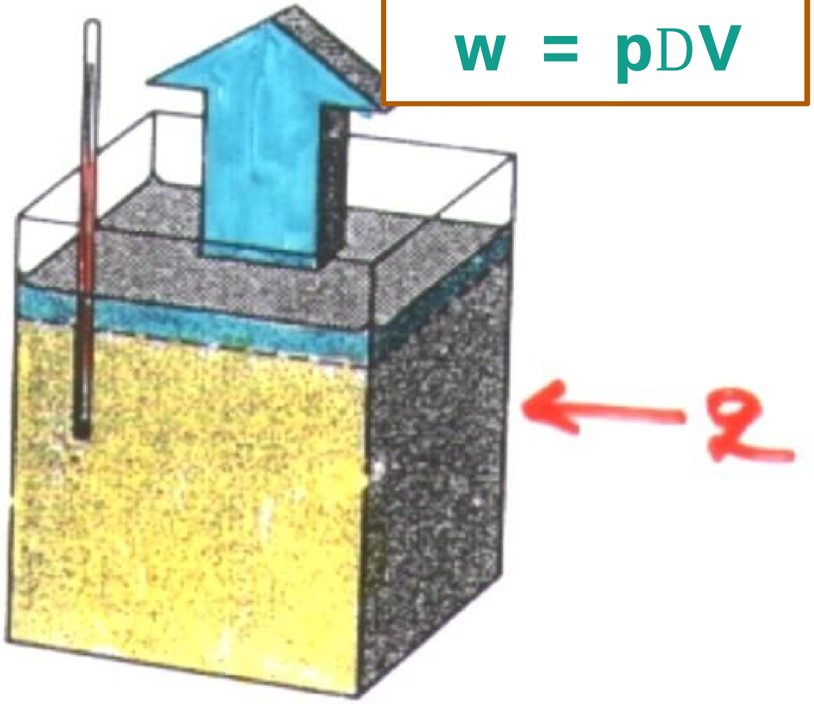
When a quantity of energy, *q,* is transferred to a *constant volume system* as heat,

the internal energy changes by $\Delta U = q$.

The *enthalpy*, H, of a system is a modification of the internal energy,

which automatically takes into account the work of expansion,

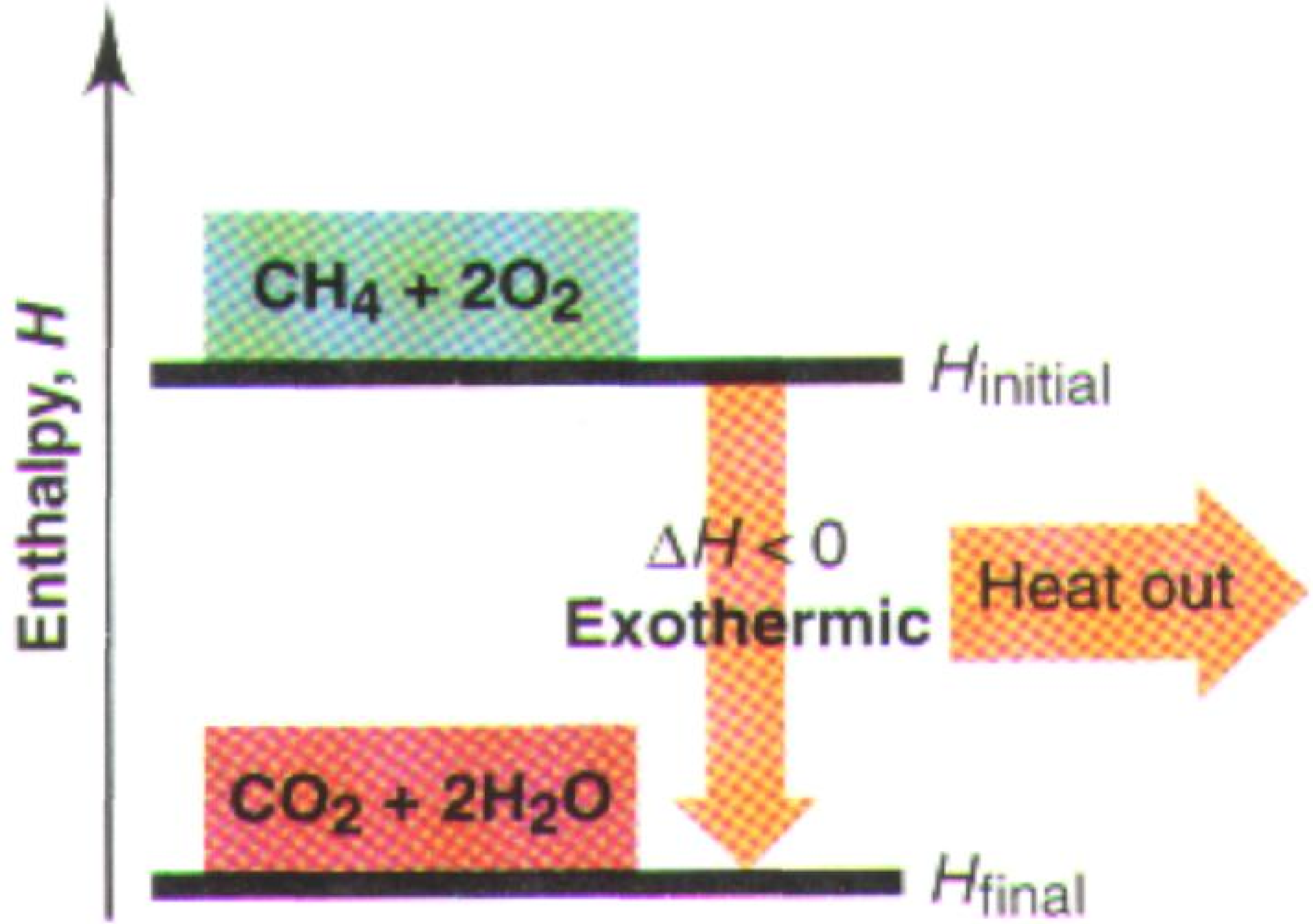
when the system is heated at constant pressure.

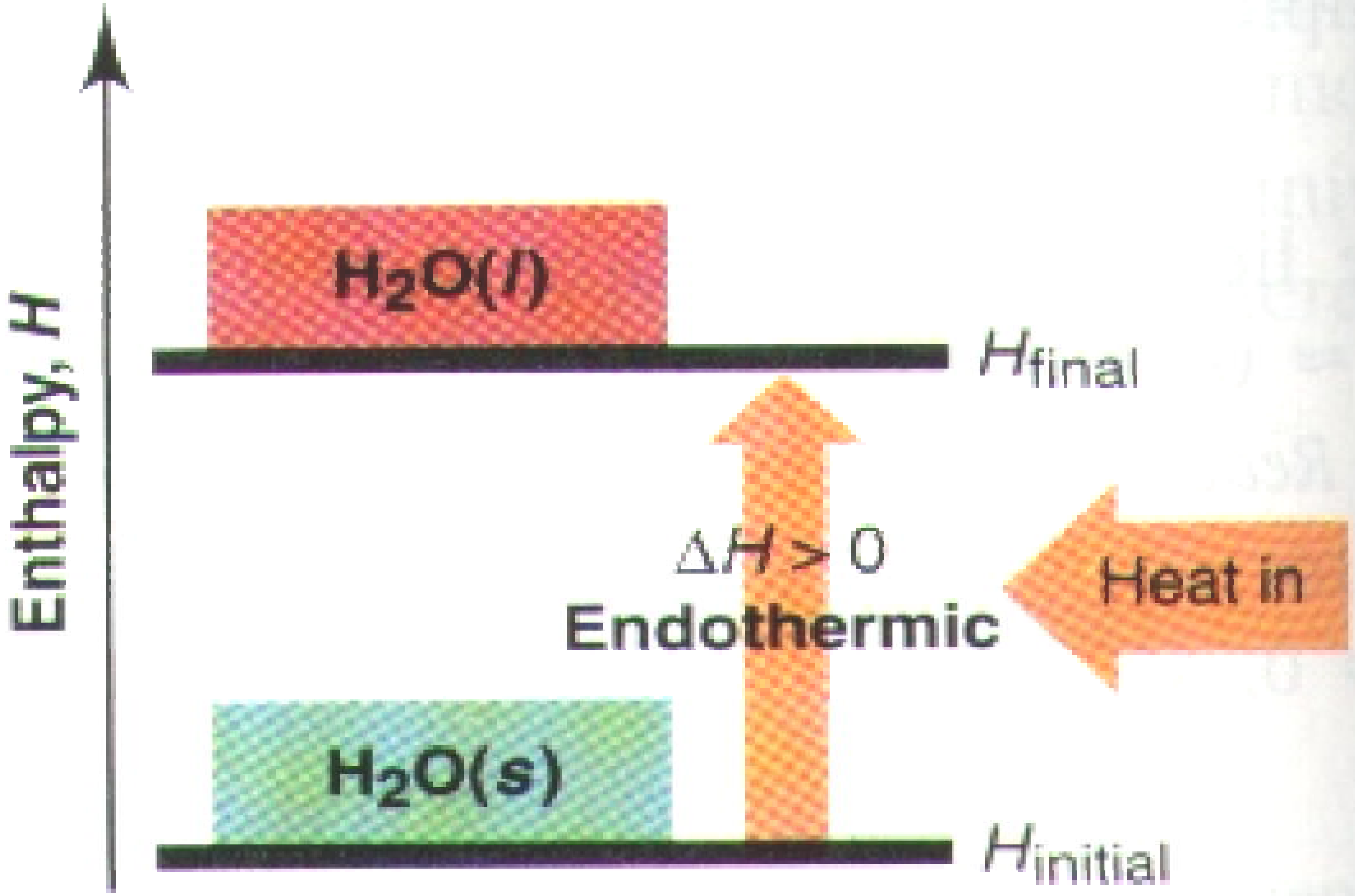


$w = p\Delta V$

$p =$ konst

$V \neq$ konst


Enthalpy, H
$CH_4 + 2O_2$
H_{initial}
$\Delta H < 0$
Exothermic
Heat out
$CO_2 + 2H_2O$
H_{final}


Enthalpy, H
$H_2O(l)$
H_{final}
$\Delta H > 0$
Endothermic
Heat in
$H_2O(s)$
$H_{initial}$

B

Enthalpies of transition
(change of phase – melting or evaporating)

- **The *molar enthalpy of melting* is the change of enthalpy that occurs when unit amount of substance of a solid melts;**

- **it is energy that has to be supplied as heat when the melting occurs at constant pressure.**

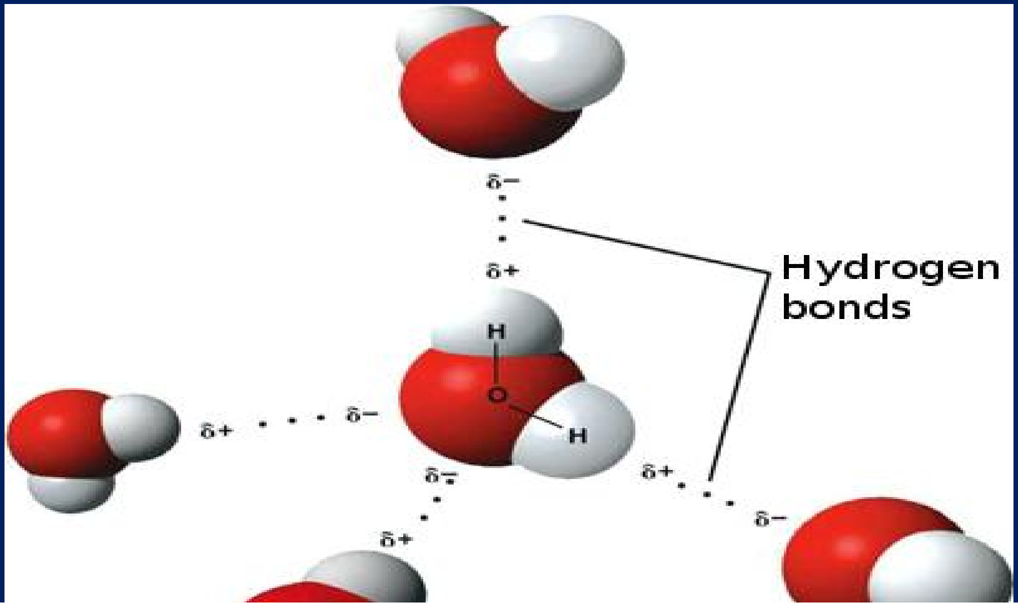
Enthalpies of transition (change of phase – melting or evaporating)

- The *molar enthalpy of vaporization* is the change of ethalpy that occurs when unit amount of substance of a liquid evaporates;
- it is energy that has to be supplied as heat when vaporization occurs at constant pressure.

Enthalpies of transition (change of phase – melting or evaporating)

$H_2O_{(s)} \rightarrow H_2O_{(l)}$ $\Delta H_{melt,m}$ = +6.0 kJ mol^{-1}

$H_2O_{(l)} \rightarrow H_2O_{(g)}$ $\Delta H_{vap,m}$ = +40.7 kJ mol^{-1}



- **Enthalpies of vaporization and melting are positive:**

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \qquad \Delta H_{melt,m} = +6{,}0\ \mathrm{kJ\ mol^{-1}}$$

- **the *enthalpy of freezing* is the negative of the enthalpy of melting:**

$$H_2O_{(l)} \rightarrow H_2O_{(s)} \qquad \Delta H = -6{,}0\ \mathrm{kJ\ mol^{-1}}$$

ENTHALPY OF SOLUTION

Enthalpy change accompanying dissolution of a salt to give an infinitely dilute solution

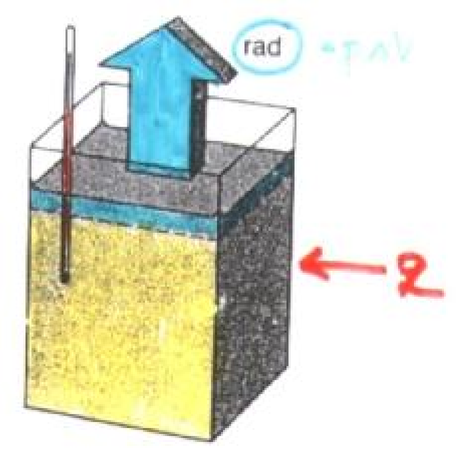
- $NaCl_{(s)} + H_2O \quad \rightarrow \qquad \Delta H = +$
- Cup cools

- **The *enthalpy of combustion* is the enthalpy change accompanying complete combustion of a sample**

- **(to carbon dioxide and water in the case of organic materials such as hydrocarbons and carbohydrates).**

Bomb calorimeter

The ***enthalpy*, H**, of a system is a modification of the internal energy, which automatically takes into account the work of expansion, when the system is heated at constant pressure.



p = const

When a quantity of energy, q, is transferred to a constant volume system as heat,

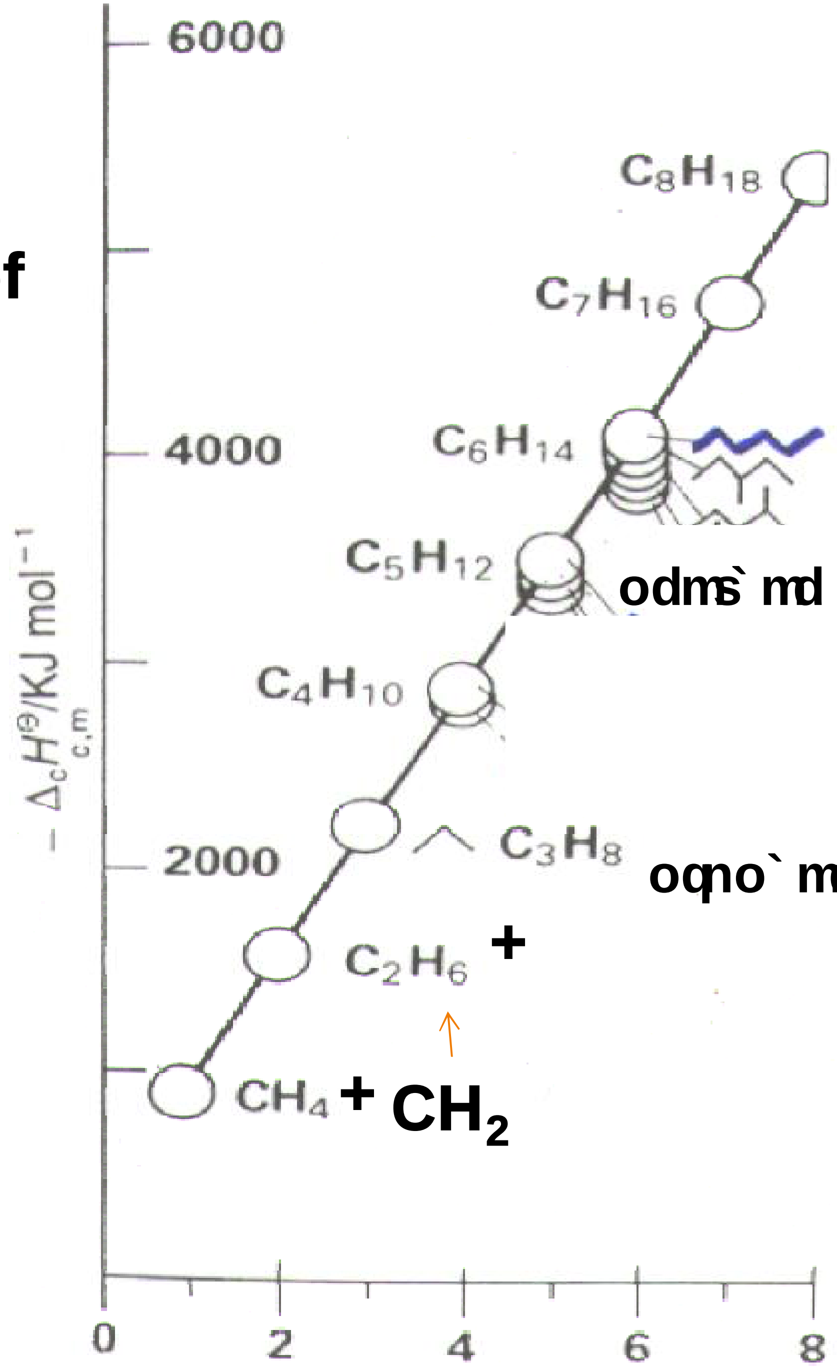
the internal energy changes by $\Delta U = q$

Does bomb calorimeter measure ΔU or ΔH?

- **The *standard state* of a substance is its most stable form under a pressure of 1 atm (101.325 kPa) at the temperature specified.**

- **The *standard enthalpy of reaction,* ΔH^o, is the enthalpy of reaction when all the reactants and all the products are in their standard states.**

The enthalpy of combustion of alkanes



The enthalpy of combustion of the alkanes increases with the number of CH_2 units

odms` md $BG_2BG_1BG_1BG_1BG_2$

oqno` md $BG_2BG_1BG_1BG_1BG_2$

+

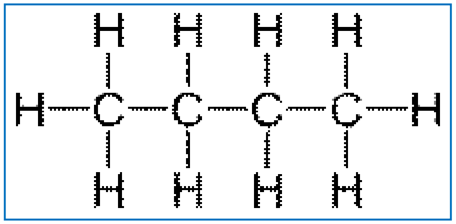
+ CH_2

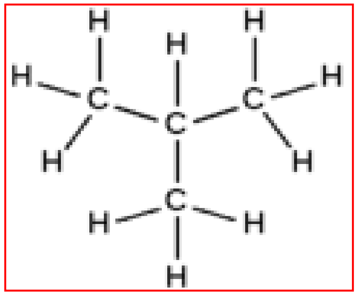
Number of carbon atoms

The enthalpy of combustion of alkanes

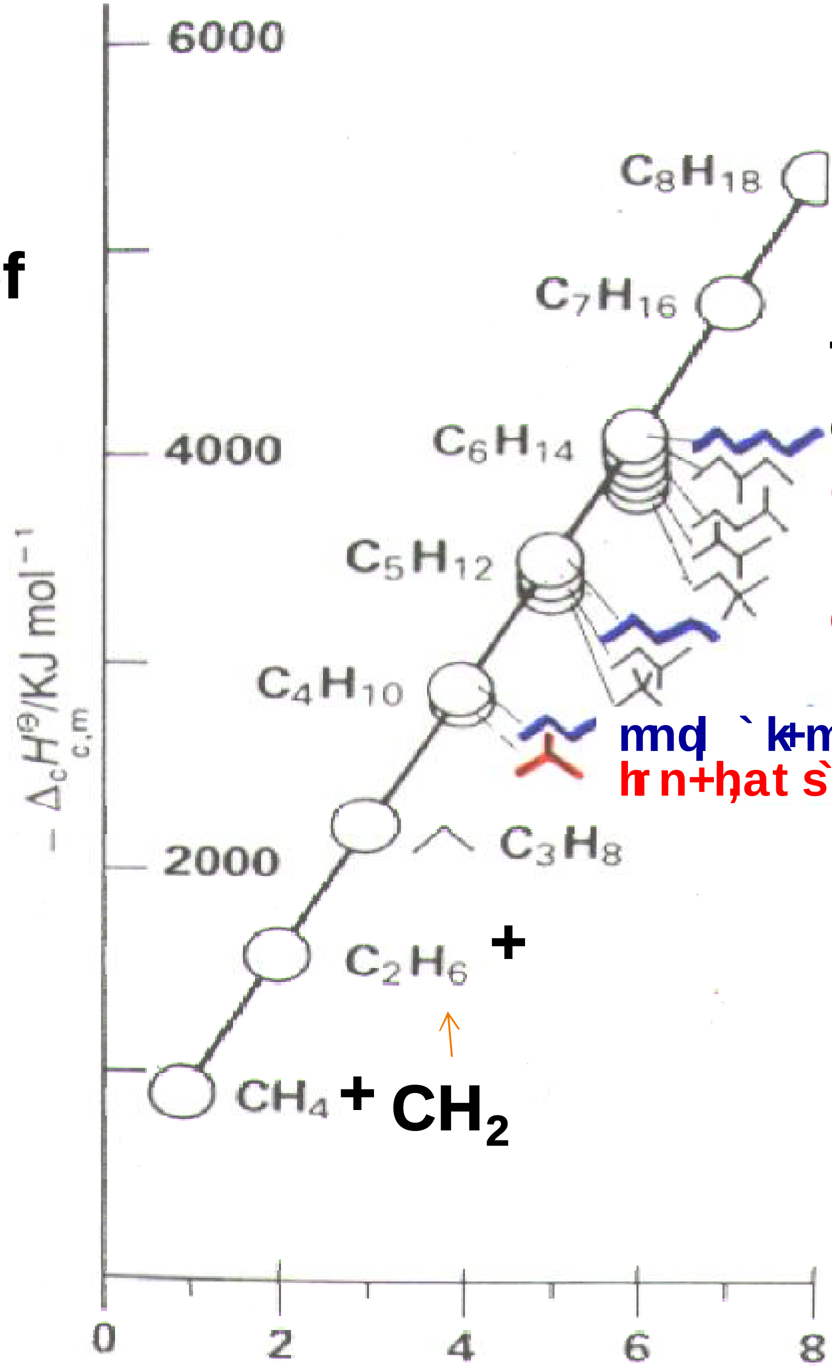
C_4H_{10} :

mnd ` k+mat s` md





hr n+hat s` md



Number of carbon atoms

The enthalpy of combustion of alkane **decreases with increased degree of chain branching**

Standard enthalpy of combustion (298,15 K)

Molecule	M_r (g mol^{-1})	$\Delta H_{c.m}^o$ (kJ mol^{-1})	$\Delta H_{c.m}^o/M$ (kJ g^{-1})
C_2H_6 ethane	30	-1560	-52
C_2H_5OH ethanol	46	-1371	-30
CH_3CHO ethanal (aldechyde)	44	-1167	-27
CH_3COOH ethanoic (acetic) acid	60	-875	-15

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(g)}$$

$$\Delta H_{c.m}{}^{o} = -2816 \text{ kJ mol}^{-1}$$

Standard enthalpy of combustion (298,15 K)

molecule	M_r	$\Delta H_{c.m}{}^{o}$ (kJ mol^{-1})	$\Delta H_{c.m}{}^{o}$ /M (kJ g^{-1})
glucose	180,16	-2816	-15,59
starch			-17,51

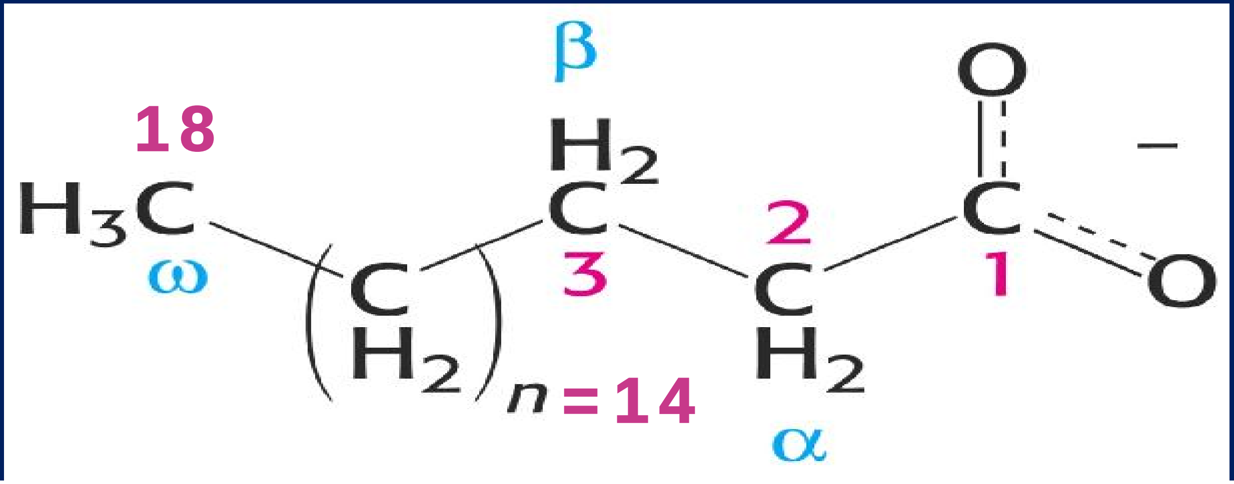
Standard enthalpy of combustion (298,15 K)

Molecule	M_r	$\Delta H_{c.m}^{o}$ (kJ mol^{-1})	$\Delta H_{c.m}^{o}$ /M (kJ g^{-1})
glycine	75,07	-978	-13,03
alanine	89,09	-1621	-18,20
leucine	131,17	-3578	-27,28

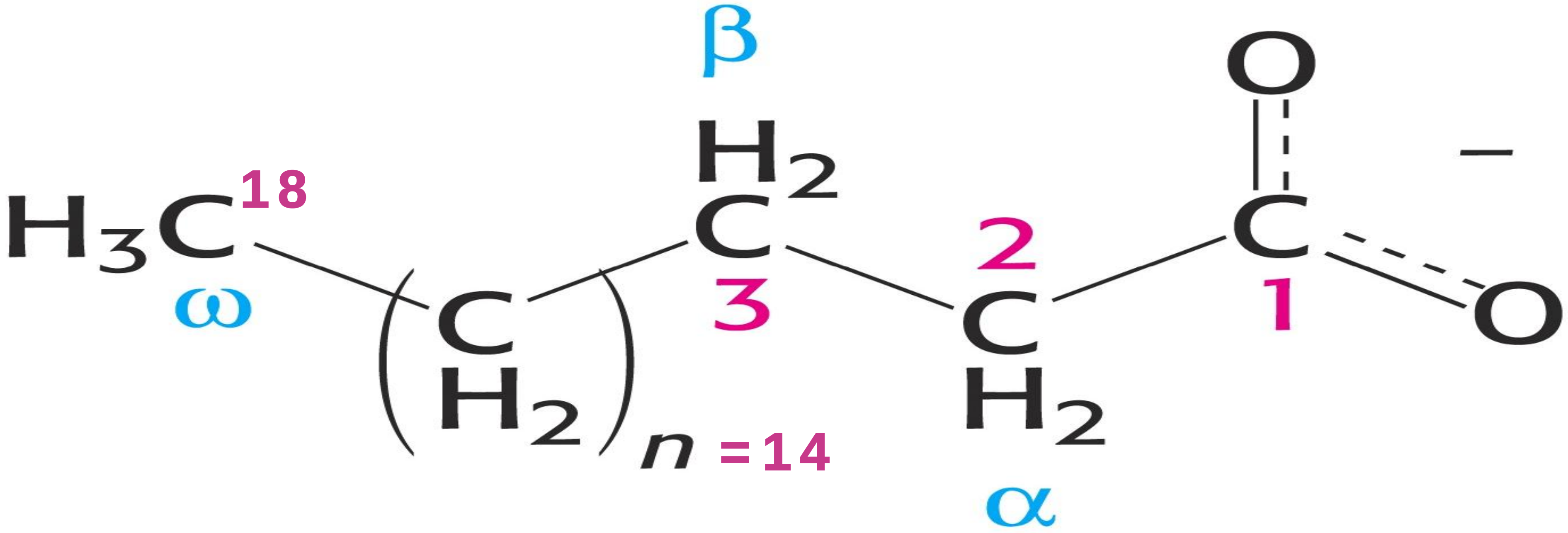
Standard enthalpy of combustion (298,15 K)

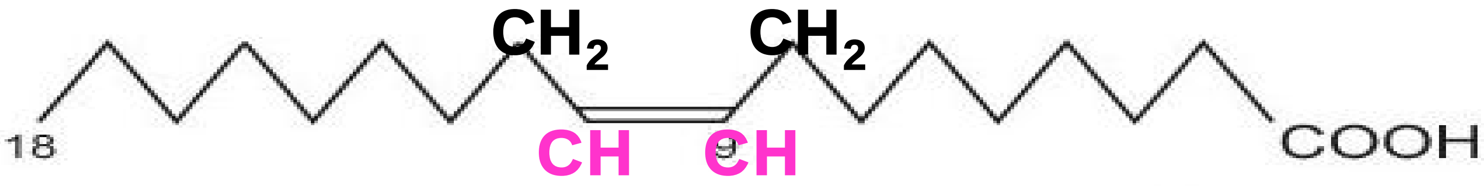
Molecule	M_r	$\Delta H_{c.m}^{o}$ (kJ mol^{-1})	$\Delta H_{c.m}^{o}$ /M (kJ g^{-1})
stearic acid	284,48	-11278	-39,64
oleic acid	282,46	-11106	-39,32

stearic acid



	M_r	$-\Delta_c H^o$ (kJ mol^{-1})
Stearic acid	284,48	11278
oleic acid	282,46	11106





oleinska kiselina (ω9, 18:1, Δ^9)

- **Stearic acid has a higher amount of the standard enthalpy of combustion compared to oleic acid, because stearic acid is more reduced**

- **Both fatty acids have 18 carbon atoms**

- **Unsaturated oleic has one double bond, or 2 hydrogen less**

- **Unsaturated bond (-CH = CH-) represents the oxidized form**
- **with respect to a saturated, reduced form** $(\text{-CH}_2\text{-CH}_2\text{-})$

carbohydrates	16 kJ/g
lipids	37 kJ/g
proteins	~ 17 kJ/g (while catabolised in organism)
	~ 21 kJ/g (combustion in bomb calorimeter)

- **Some catabolic reactions (oxidation = decomposition reaction) in the human body needs to invest energy**

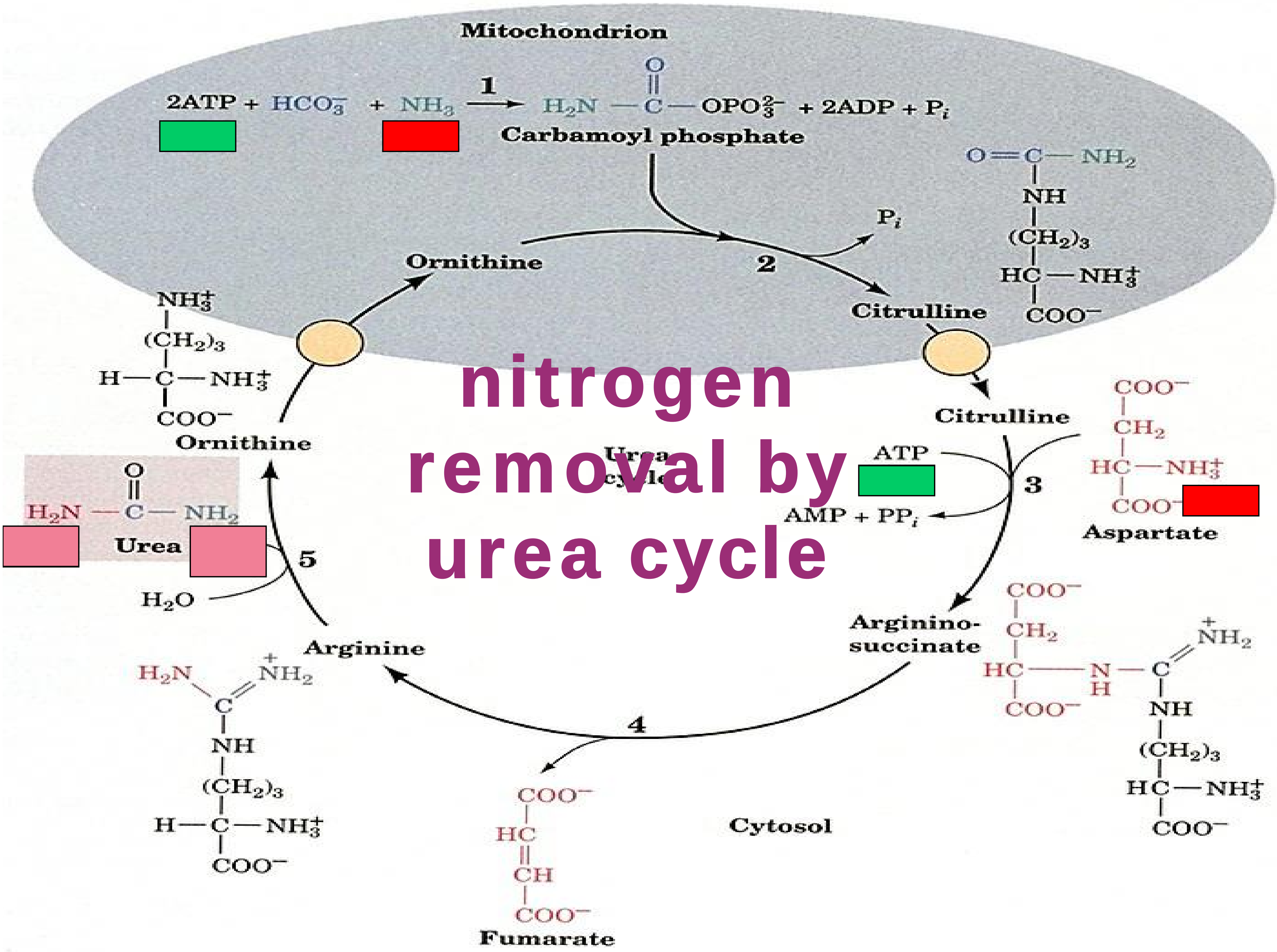
- **In catabolic reactions of fats and carbohydrates in the body, small (negligible) amount of energy (ATP) is needed**
- **and the data obtained in the bomb calorimeter approximately correspond to those used in nutritional calculations**

- However, in calculating the mass of the protein needed for the organism
- we have to calculate with the lower amount of energy than that obtained in a bomb calorimeter
- because the removal of 2 nitrogens from amino acids requires 3 ATP molecules

- That means, a considerable amount of energy has to be invest in protein degradation

- So the net energy released in the oxidation of 1 g protein in the body is 17 kJ (not 21 kJ)

nitrogen removal by urea cycle



- **The standard molar *enthalpy of formation*, $\Delta H^{o}_{f,m}$**
- **is the enthalpy change accompanying formation of unit amount of the compound from its elements,**
- **all components being in their standard states.**

Enthalpies of formation

$$6C_{(s)} + 6H_{2(g)} + 3O_{2(g)} \circledR C_6H_{12}O_{6(s)} \qquad \Delta H_{f.m}^{o} = ?$$

$$2A + B \circledR C$$

$$DH^{o} = \Delta H_{f.m}^{o}\,(C) - [2\,\Delta H_{f.m}^{o}\,(A) + \Delta H_{f.m}^{o}\,(B)]$$

$$2A + B \text{ ® } C$$

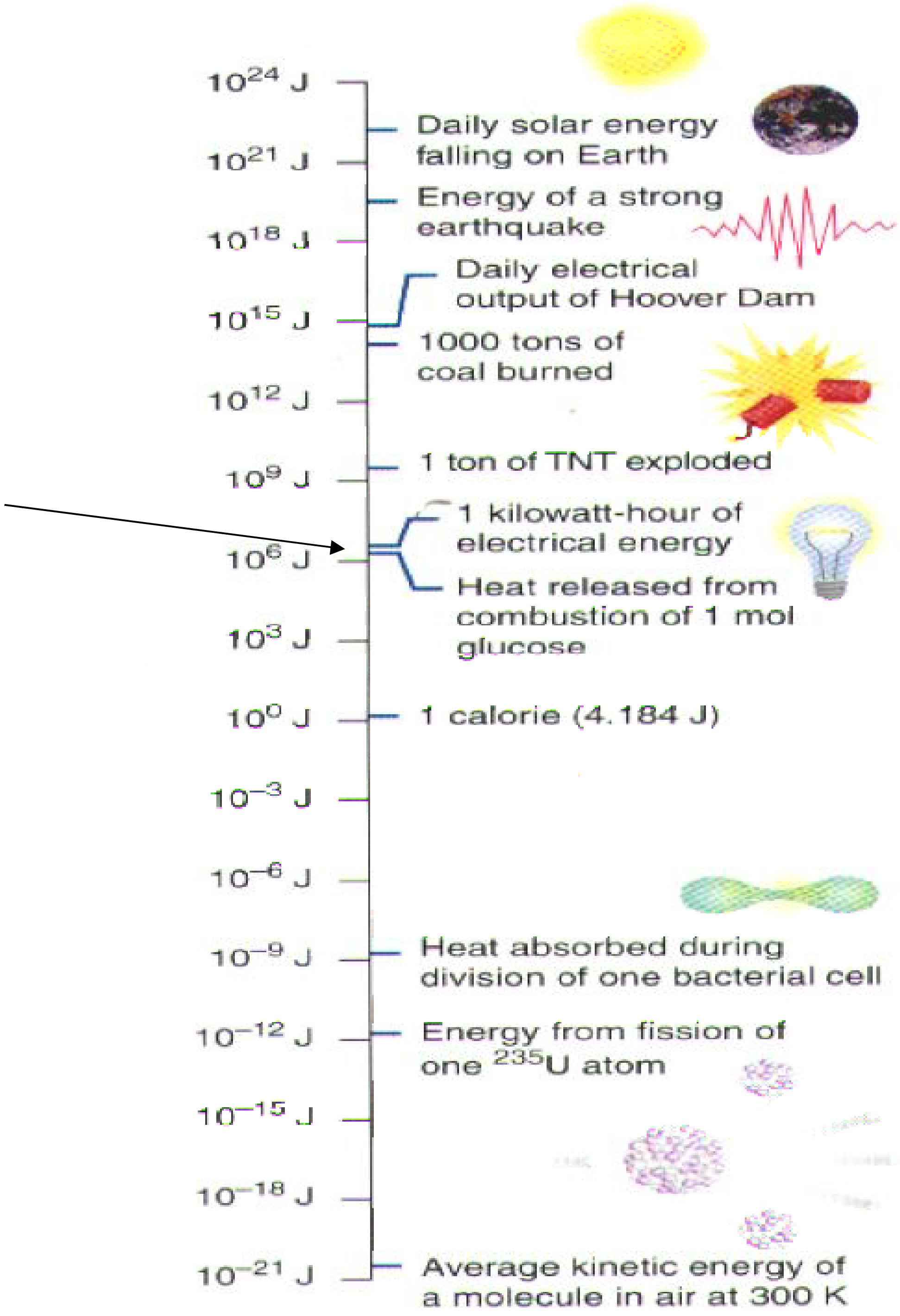
$$\mathrm{D}H^{o} = \Delta H_{f.m}{}^{o}\ (C) - [2\ \Delta H_{f.m}{}^{o}\ (A) + \Delta H_{f.m}{}^{o}\ (B)]$$

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(g)};\ \Delta H^{o} = -2816\ \mathrm{kJmol^{-1}}$$

$$\Delta H^{o} = 6\ \Delta H_{f.m}{}^{o}(H_2O)\ _{(s)} + 6\ \Delta H_{f.m}{}^{o}(CO_2) - \Delta H_{f.m}{}^{o}(C_6H_{12}O_6)$$

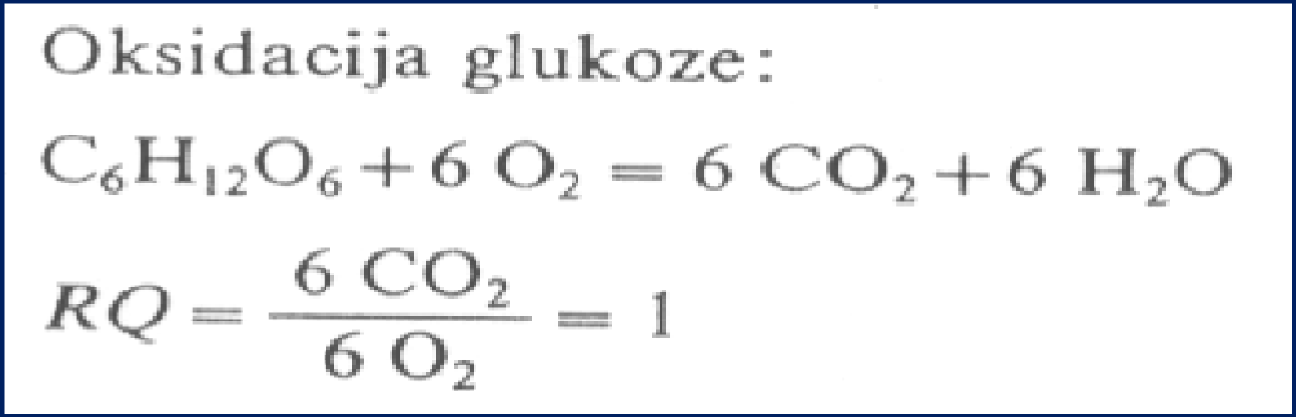
$$-2816\ \mathrm{kJ\ mol^{-1}} = 6(-285{,}8\ \mathrm{kJ\ mol^{-1}}) + 6(-393{,}5\ \mathrm{kJ\ mol^{-1}}) - \Delta H_{f.m}{}^{o}$$

$$\Delta H_{f.m}{}^{o}(C_6H_{12}O_6) = -1268\ \mathrm{kJ\ mol^{-1}}$$


10^{24} J
Daily solar energy falling on Earth
10^{21} J
Energy of a strong earthquake
10^{18} J
Daily electrical output of Hoover Dam
10^{15} J
1000 tons of coal burned
10^{12} J
1 ton of TNT exploded
10^{9} J
1 kilowatt-hour of electrical energy
10^{6} J
Heat released from combustion of 1 mol glucose
10^{3} J
10^{0} J
1 calorie (4.184 J)
10^{-3} J
10^{-6} J
Heat absorbed during division of one bacterial cell
10^{-9} J
Energy from fission of one ^{235}U atom
10^{-12} J
10^{-15} J
10^{-18} J
Average kinetic energy of a molecule in air at 300 K
10^{-21} J

Respiration quotient

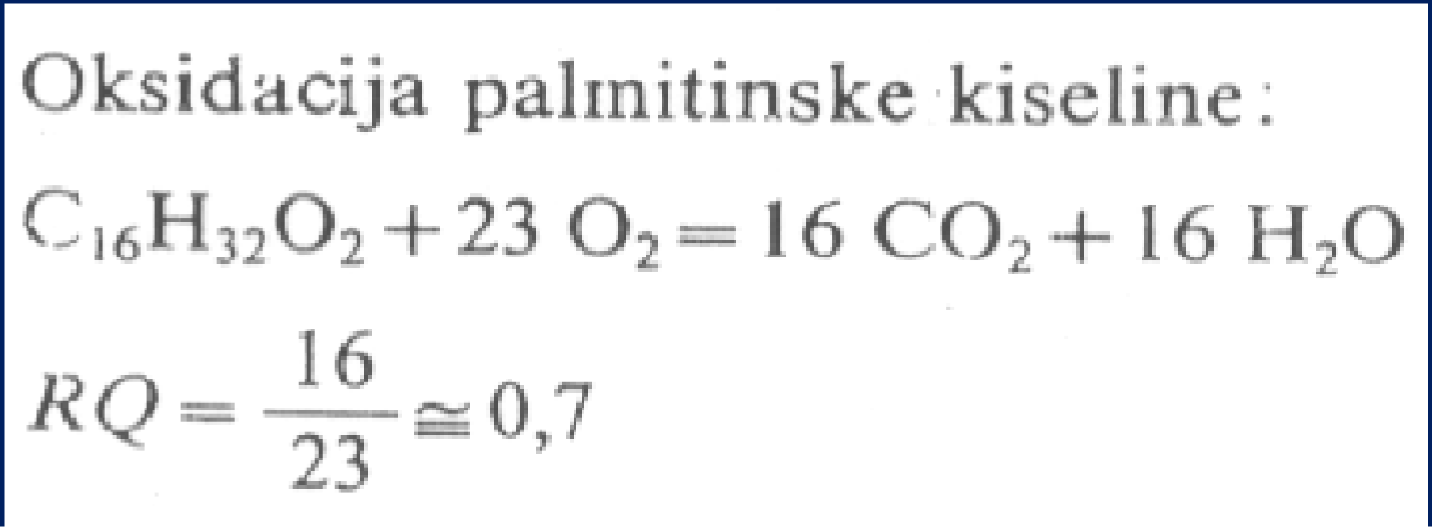
RQ = V(formed CO_2)/V(consumed O_2)



Oksidacija glukoze:

$$C_6H_{12}O_6 + 6\ O_2 = 6\ CO_2 + 6\ H_2O$$

$$RQ = \frac{6\ CO_2}{6\ O_2} = 1$$



Oksidacija palmitinske kiseline:

$$C_{16}H_{32}O_2 + 23\ O_2 = 16\ CO_2 + 16\ H_2O$$

$$RQ = \frac{16}{23} \cong 0,7$$

- A few hours after a meal glucose is the main fuel in all tissues

  This is manifested as an increase in respiratory quotient

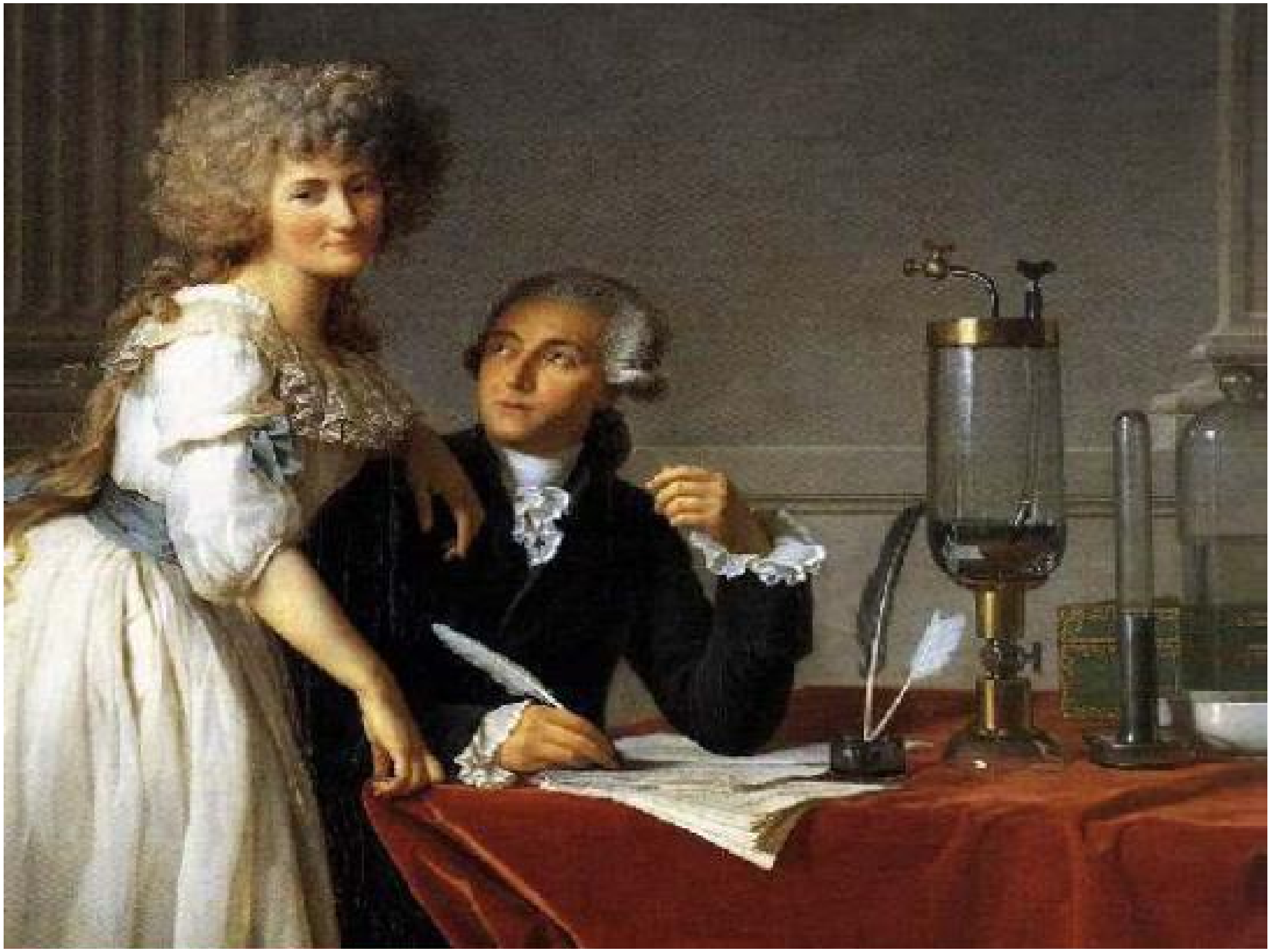
  of 0.8 in the fasting state to nearly 1

Energy yields, oxygen consumption, and carbon dioxide production in the **oxidation of metabolic fuels**

	Energetsko iskorištenje (kJ/g)	Utrošeni O_2 (l/g)	Stvoreni CO_2 (l/g)	RQ	Energija (kJ)/l O_2
carbohydrates	16	0,829	0,829	**1,00**	20
proteins	17	0,966	0,782	0,81	20
lipids	37	2,016	1,427	0,71	20
alcohol	29	1,429	0,966	0,66	20

Lavoisier (18. century) studying human respiration as a form of combustion

He measured substances consumed and excreted in addition to changes in heat to understand the chemical nature of respiration



- Atkins, problem 4. Suppose you were caught on a mountain with soaking wet clothes;
- What energy would your body have to supply if the wind caused the evaporation of 500 g of water?

500 g H_2O

$H_2O_{(l)} \rightarrow H\ _2O_{(g)}$ $\Delta H_{vap,m}$ = +40.7 kJ mol^{-1}

n = 500 g / 18 g mol^{-1} = 27.8 mol

$\Delta H = 40.7 \cdot 12.8 = 1130.6$ kJ

- Problem 5. Foostuffs are often classified as “so many Calories”:
- Given that 1 Calorie (as used by dieticians) = 4.18 kJ,
- calculate the mass of cheese that must be consumed in order to offset the energy loss in the problem 4,
- given that the calorific value of cheese is 5 Calories per gram
    - 1 g cheese $\Leftrightarrow$ 5 Cal
    - 1 Cal $\Leftrightarrow$ 4.18 kJ

    - 1 g cheese $\Leftrightarrow$ $5 \cdot 4.18 = 20.9$ kJ
    - x g cheese $\Leftrightarrow$ 1130.6 kJ
    - $x = 1130.6 \text{ kJ} / 20.9 \text{ kJ g}^{-1} = 54 \text{ g}$

At the end of statement write YES or NO

The system containing the ice is poorer in energy then the same system after melting the ice to water

YES

The relationship between the amount of heat that is released into the environment by combustion of 1 mol of alkanes is $\Delta_c H(CH_4) < \Delta_c H(C_2H_6)$

YES

At the end of statement write YES or NO

The enthalpy of combustion of alkane increases with decrease of the number of CH_2 units

$BG_2BG_1BG_1BG_1BG_2$ $BG_2BG_1BG_2$
(pentane vs propane)

NO

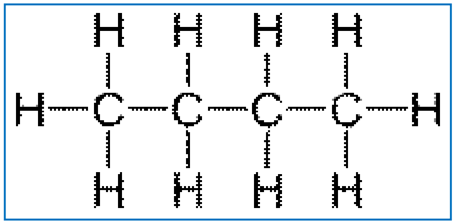
The system containing the ice (= 1 mol solid H_2O) is equal in energy content to the system containing 1 mol liquid H_2O

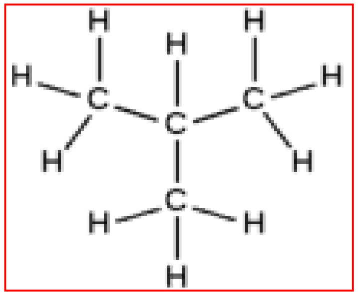
NO

The enthalpy of combustion of alkanes

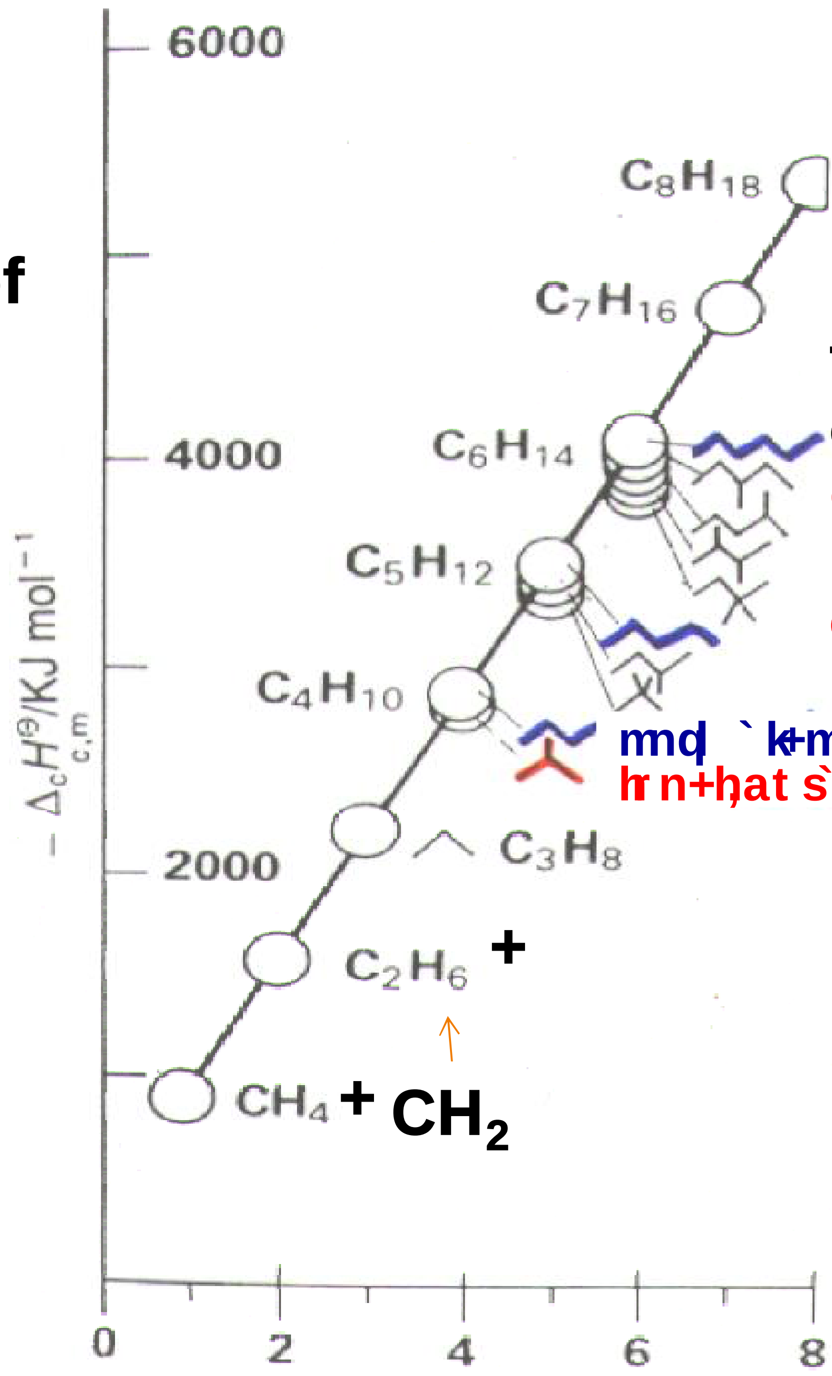
C_4H_{10} :

mnql ` k+mat s` md





hr n+hat s` md



CH_2

mnql ` k+mat s` md $BG_2BG_1BG_1BG_2$

hr n+hat s` md

Number of carbon atoms

The enthalpy of combustion of alkane **decreases with increased degree of chain branching**

At the end of statement write YES or NO

The equation of the first law of thermodynamics includes plus amount of work if the work is done on the system

YES

Enthalpy of formation is easily and directly determined in bomb calorimeter

NO