

# **CHEM103**

# **General Chemistry**

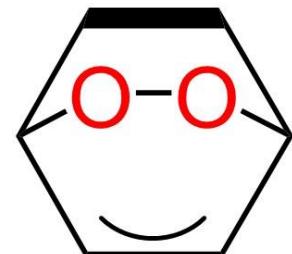
## **Chapter 5: Thermochemistry**

(热化学)



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# **Assignments 3-4 & Mid-term EXAM**

Please submit your assignments to any of your TAs or me during the classes. Or you can submit your assignment to the folder **outside room 520, research building 1** (anytime you like).

## **Homework 3**

**Due date: 21 Sep. (Wed)**

## **Homework 4**

**Due date: 28 Sep. (Wed)**

## **Mid-term EXAM**

**13 Nov. 10-12 AM (Sun)**

# HW1

3. An air sample consists of oxygen and nitrogen gas as major components. It also contains carbon dioxide and traces of some rare gases. All these gases are evenly distributed throughout the sample of air.

Which term or terms could be used to describe this sample of air?

- i)** mixture; **ii)** heterogeneous mixture; **iii)** homogenous mixture; **iv)** solution; **v)** pure substance; **vi)** compound; **vii)** element

A) i and ii

B) i and iii form homogeneous mixtures [Figure 1.8(b)]. Homogeneous mixtures are also called

C) i, iii and iv **solutions**. Although the term *solution* conjures an image of a liquid, solutions can be

D) v and vi solids, liquids, or gases.

E) v and vii

$$11C: 547 * (1894 - 7.89 * 154)$$

$$= 547 * (1894 - 1220)$$

$$= 547 * (680)$$

$$= 3.7 * 10^5$$

# **Review on Chapter 4**

**(Aqueous) Solution, Solvent, Solute**

**Dissociation:** (Strong & Weak) Electrolyte; Conductivity

**Precipitation:** Solubility; Metathesis (Exchange) Reactions; Molecular and (Net) Ionic Equations

**Acid-Base:** Arrhenius/Brønsted Acids & Bases; Neutralization; Salt; Gas-forming Reactions

**Oxidation-Reduction (Redox) Reaction:** Oxidation numbers; Displacement Reactions; Activity Series

**Concentration:** Molarity; Dilution; Titration

# **Outline of Chapter 5**

**Thermochemistry:** energy changes involving heat in chemical reactions

**Energy:** Work & Heat; Potential Energy & Kinetic Energy; System & Surroundings

**The 1<sup>st</sup> law of Thermochemistry:** Conversation of Energy; Internal energy; Endothermic & Exothermic; State function & Path function

**Enthalpy:** Enthalpy of Reaction; Calorimetry; Heat Capacity; Hess's Law; (Standard) Enthalpy of Formation

# Energy

Thermochemistry studies the relationships between **chemical reactions** & **energy changes** involving **heat**; (thermodynamics (热力学): “therme” & “dynamis” mean “heat” & “power” in Greek, respectively).

Energy has the ability to (1) **do work** (功) and/or (2) **transfer heat** (热).

- Energy used to **move** an object having mass is called **work** (e.g. a motor, lift).
- Energy used to cause the **temperature** of an object to **rise** is called **heat** (e.g. an electric heater).



# Kinetic Energy (动能)

Kinetic energy (K.E.) for **motion** of an object  
(m: mass; v: velocity):

$$E_k = \frac{1}{2} mv^2$$

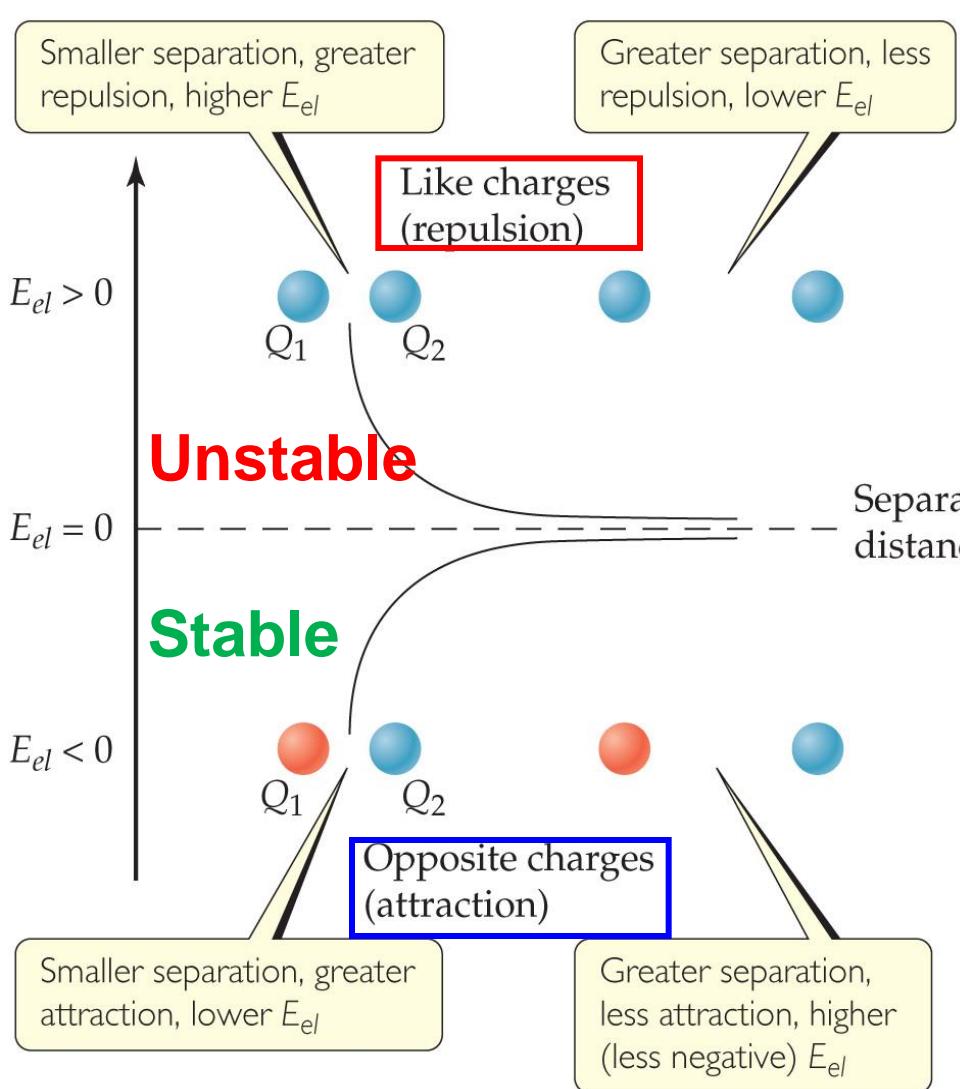


High potential energy,  
zero kinetic energy



**Decreasing** potential energy,  
**increasing** kinetic energy

# Potential Energy (勢能)



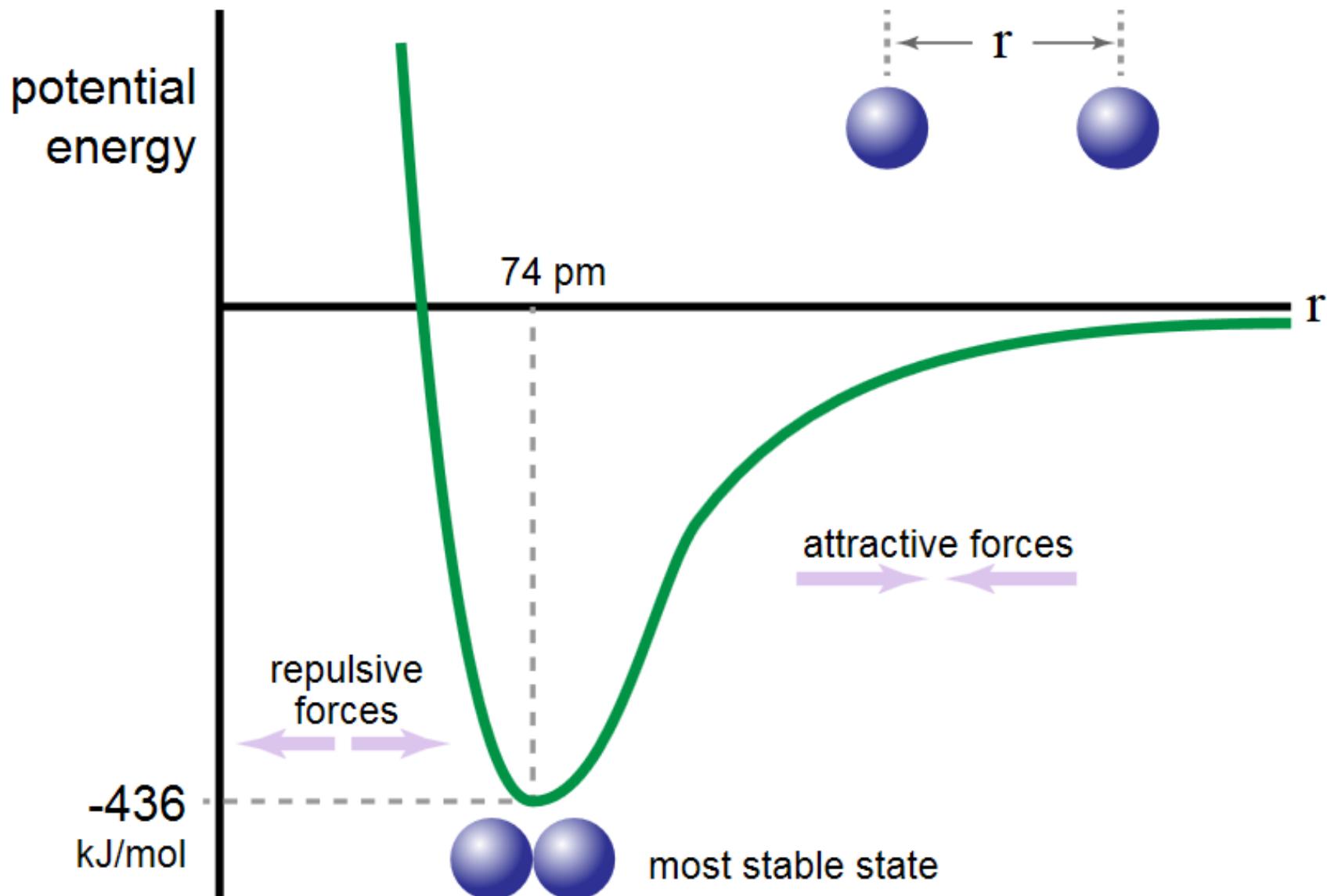
- Potential energy (P.E.): an object possesses by virtue of its **position** or **chemical composition (bonding)**.

- The most important form in ions is **electrostatic potential energy**,  $E_{el}$ :

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

$Q_1, Q_2$  = charged objects  
 $K$  = constant =  $8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$   
 $C$  = coulomb;  $J$  = joule

# Potential Energy for H<sub>2</sub>



P.E. of H<sub>2</sub> stored in a chemical bond (Chapter 8).

# Units of Energy

- The common unit of energy is **joule (J 焦耳)**:

$$1 \text{ J} = 1 \frac{\text{kg m}^2}{\text{s}^2}$$

$$E_k = \frac{1}{2} mv^2$$

- An older unit is still widely used: **calorie (cal 卡路里)**.

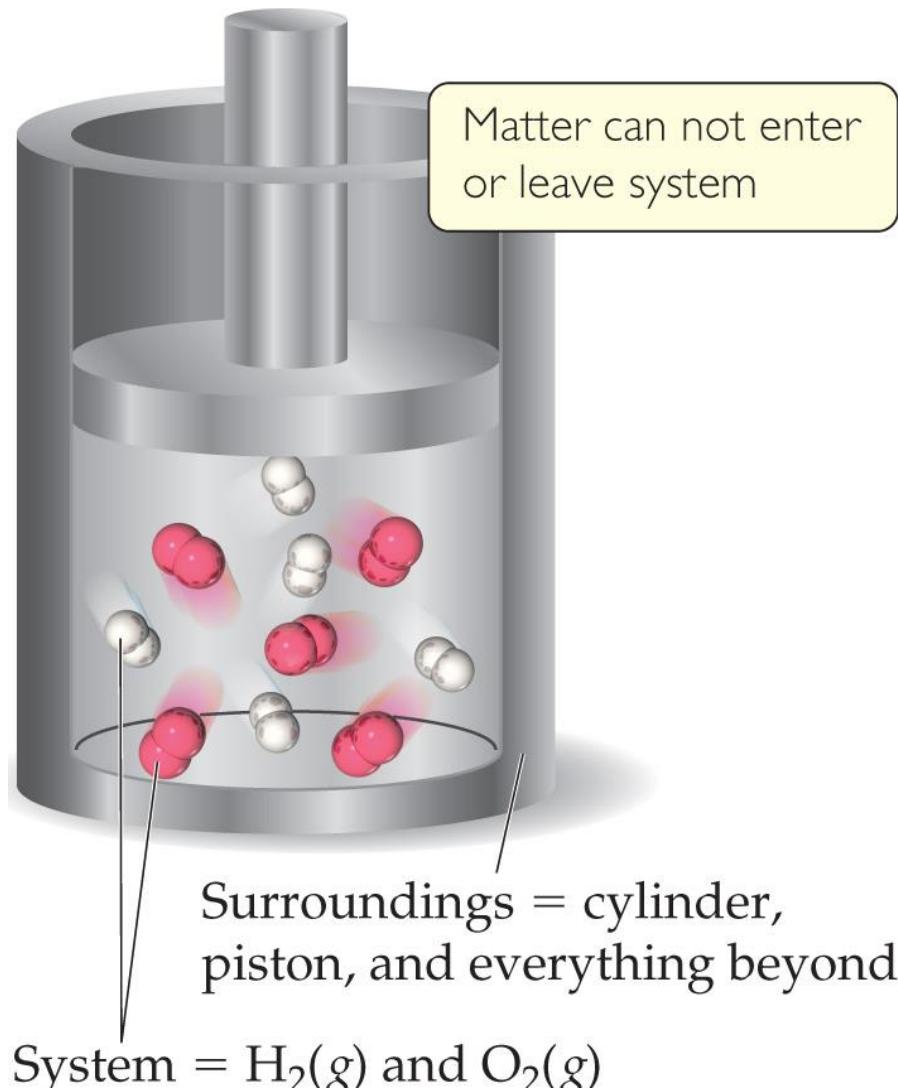
$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ kcal} = 4.184 \text{ kJ} = 4184 \text{ J}$$

1 cal: the energy needed to **increase** the temperature of **1 gram of water by 1 °C** at standard atmospheric pressure.

# System (系统) and Surroundings (环境)

Energy can enter or leave system as heat or as work done on piston



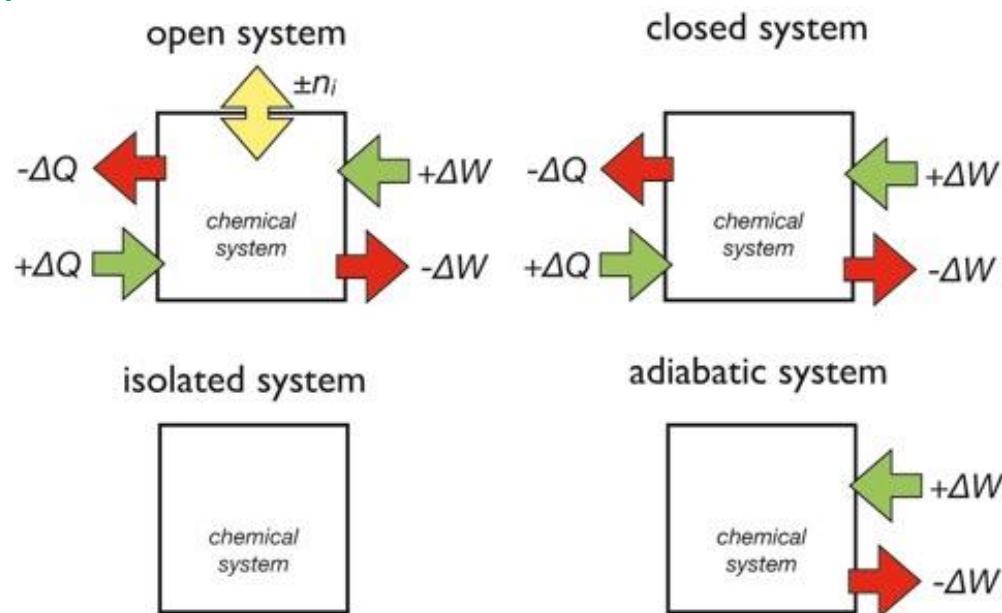
**System:** the part of the universe we study (here, H<sub>2</sub> and O<sub>2</sub> molecules).

**Surroundings** (or environment): **everything except system** (e.g. the cylinder (气缸) and piston (活塞)).

**Closed System:** Energy (E) can enter or leave system (exchanging with surrounding), but **not matter** (N, number of matter i.e.  $N_{\text{system}}$  is **constant**).

**Open System:** Energy & **matter** can enter or leave system (exchanging with surrounding).

**Isolated System:** Energy & **matter** can **NOT** enter or leave system (**NOT** exchanging with surrounding,  $E_{\text{system}}$  &  $N_{\text{system}}$  are **constant**).



# Mechanical Equivalent of Heat (热功当量)

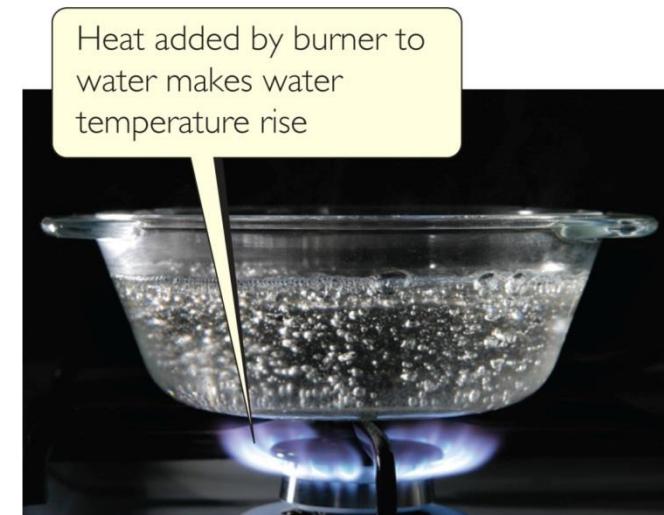
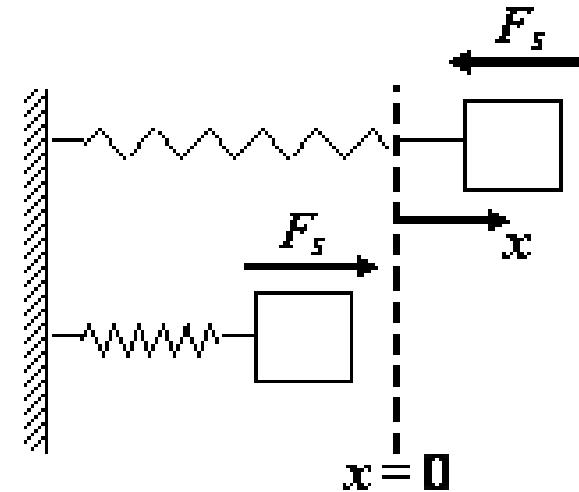
## - Relationship between Work & Heat

**Work ( $w$ ):** the energy used to **move an object** having mass over some **distance (d)** **against** a **force (F)**.

$$w = F \times d$$

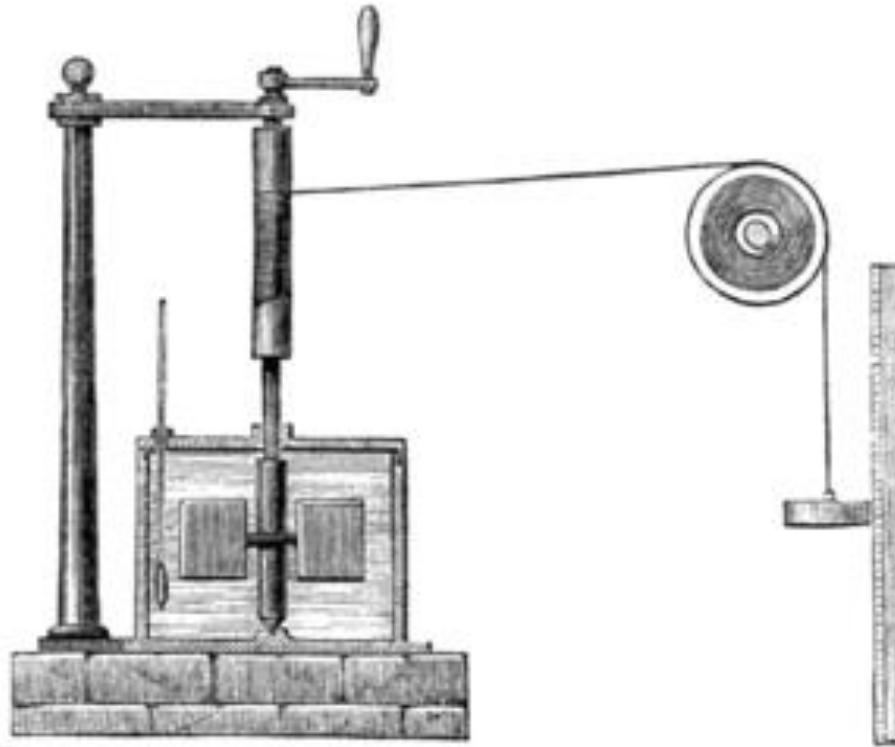
**Heat ( $q$ ):** the energy is **transferred** from a hotter object to a colder one.

(**Energy:** the **capacity/ability** to do work and/or to transfer heat.)



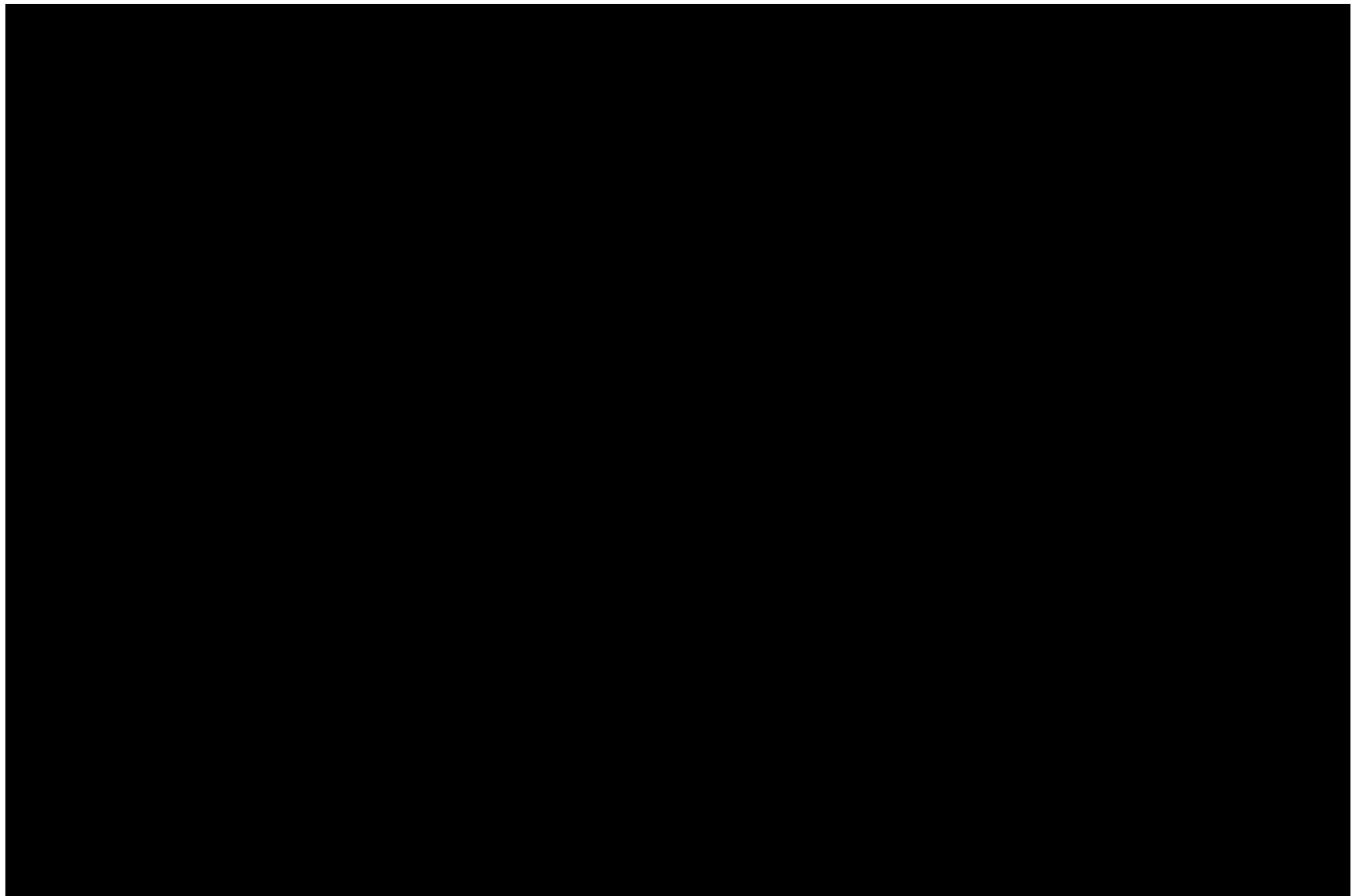
# Relationship between Work (w) & Heat (q)

$$1 \text{ cal} = 4.184 \text{ J}$$



Joule's apparatus for measuring the mechanical equivalent of heat in which the "**work**" of the falling weight is converted into the "**heat**" in the water.

# **Model of Joule's apparatus for the mechanical equivalent of heat**



“In the history of science, the **mechanical equivalent of heat** was a concept that had an important part in the development and acceptance of the **conservation of energy** and the establishment of the science of **thermodynamics** in the 19th century.”

The concept “stated that **motion** and **heat** are **mutually interchangeable** and that in every case, a **given amount** of **work** would generate the **same amount of heat**, provided the work done is totally converted to heat energy.”

From Wiki

# Conversion of Energy



High potential energy,  
zero kinetic energy



Decreasing potential energy,  
increasing kinetic energy

Energy can be converted from one type to another type (e.g. P.E. to K.E. or K.E. to P.E.).

# First Law of Thermodynamics

Energy is **neither** created **nor** destroyed.

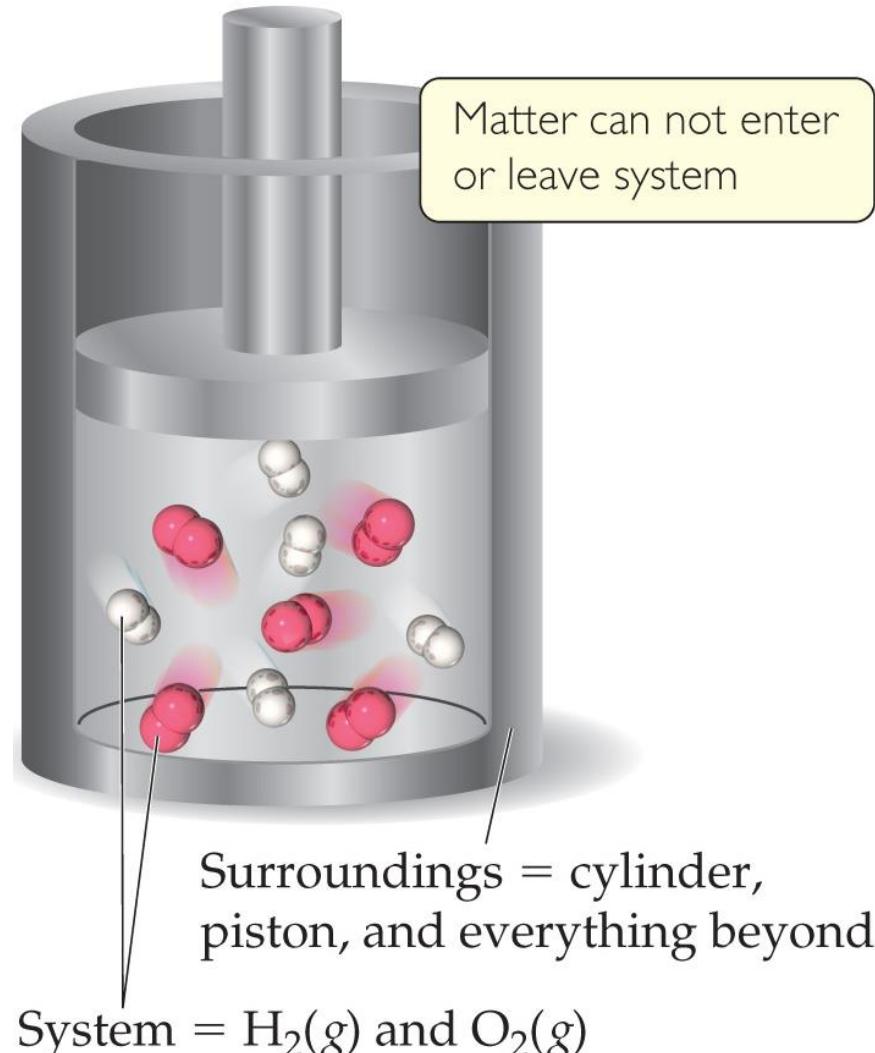
In other words, the **total energy** of the universe (**system + surroundings**) is a **constant**.

If the **system loses energy**, the **surroundings must gain energy**, and *vice versa* (反之亦然, the other way around).

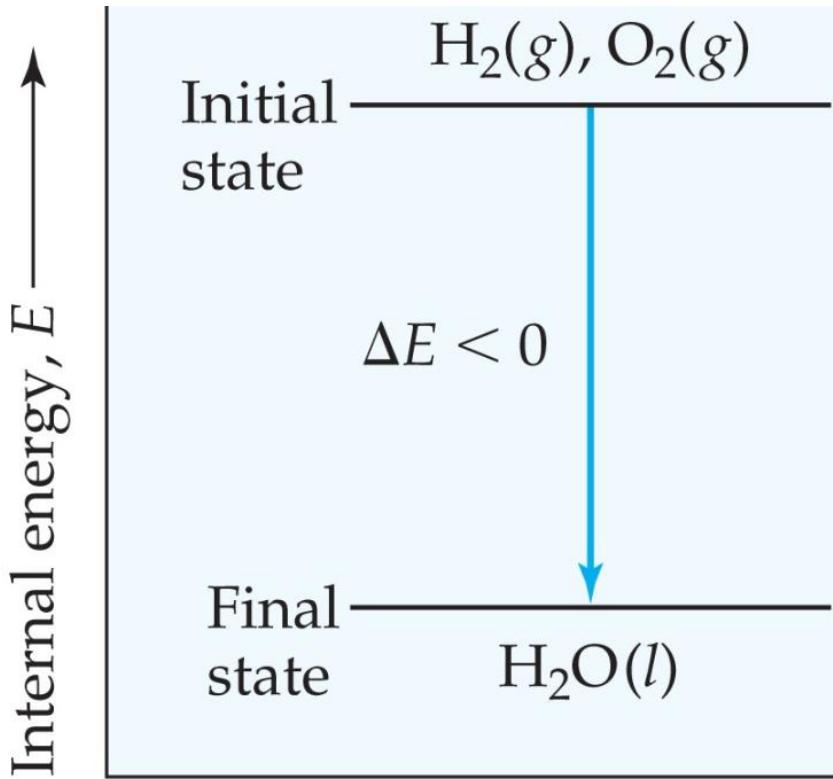
# Internal Energy (内能)

The **internal energy** ( $E$ ) of a system is the **sum of all kinetic & potential energies** of all components of the **system**.

We cannot know or determine **absolute** internal energy, **but changes** in internal energy (or **relative** internal energy)  $\Delta E$ .



# Change in Internal Energy



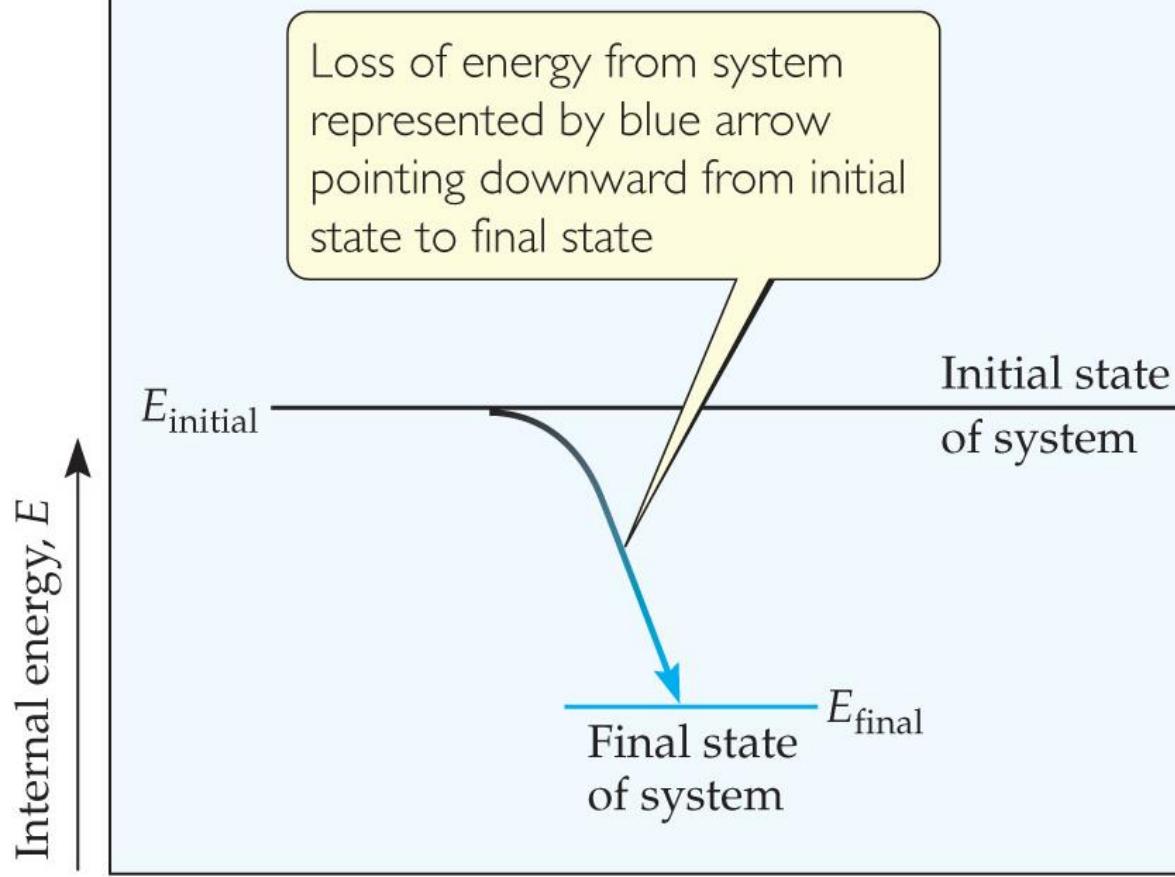
By definition, **the change in internal energy**,  $\Delta E$ , is the final energy of the system minus the initial energy of the system (a state function 状态函数):

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

**State function:** a **quantity depends only on the current state**, but not on how the system came to be in that state (**not depends on process or path**).

$$\Delta E(A+B \rightarrow D) = E_D - E_{A+B}$$

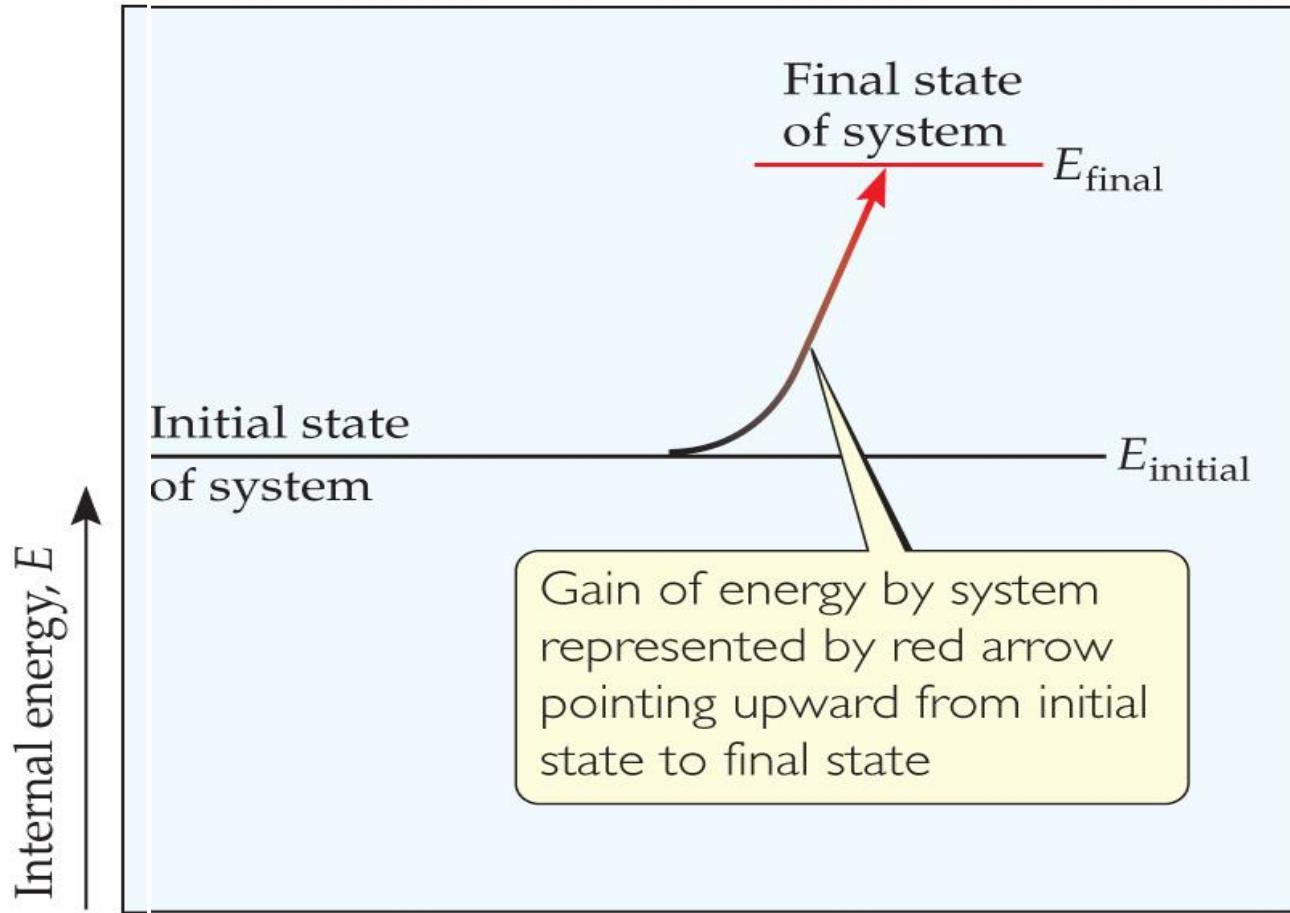
$$\Delta E(A+B \rightarrow C \rightarrow D) = E_D - E_{A+B}$$



Energy lost to surroundings,  
internal energy of system  
decreases,  $\Delta E$  negative

If  $E_{\text{final}} < E_{\text{initial}}$ ,  $\Delta E < 0$ ,

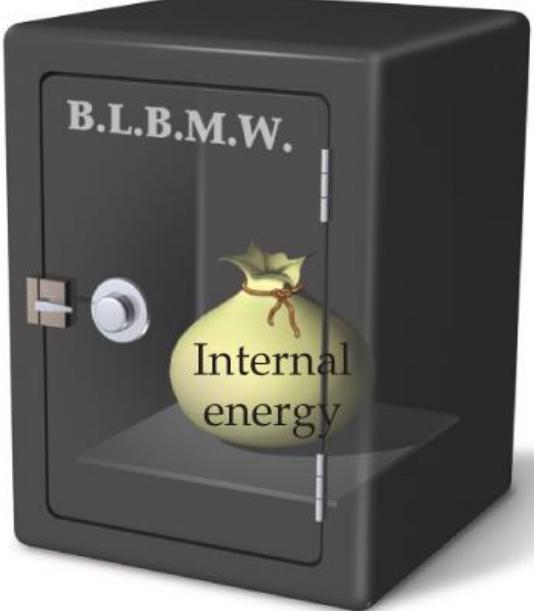
→ the **system releases** energy to the **surroundings**. (放能)



Energy gained from surroundings, internal energy of system increases.  $\Delta E$  positive

If  $E_{\text{final}} > E_{\text{initial}}$   $\Delta E > 0$

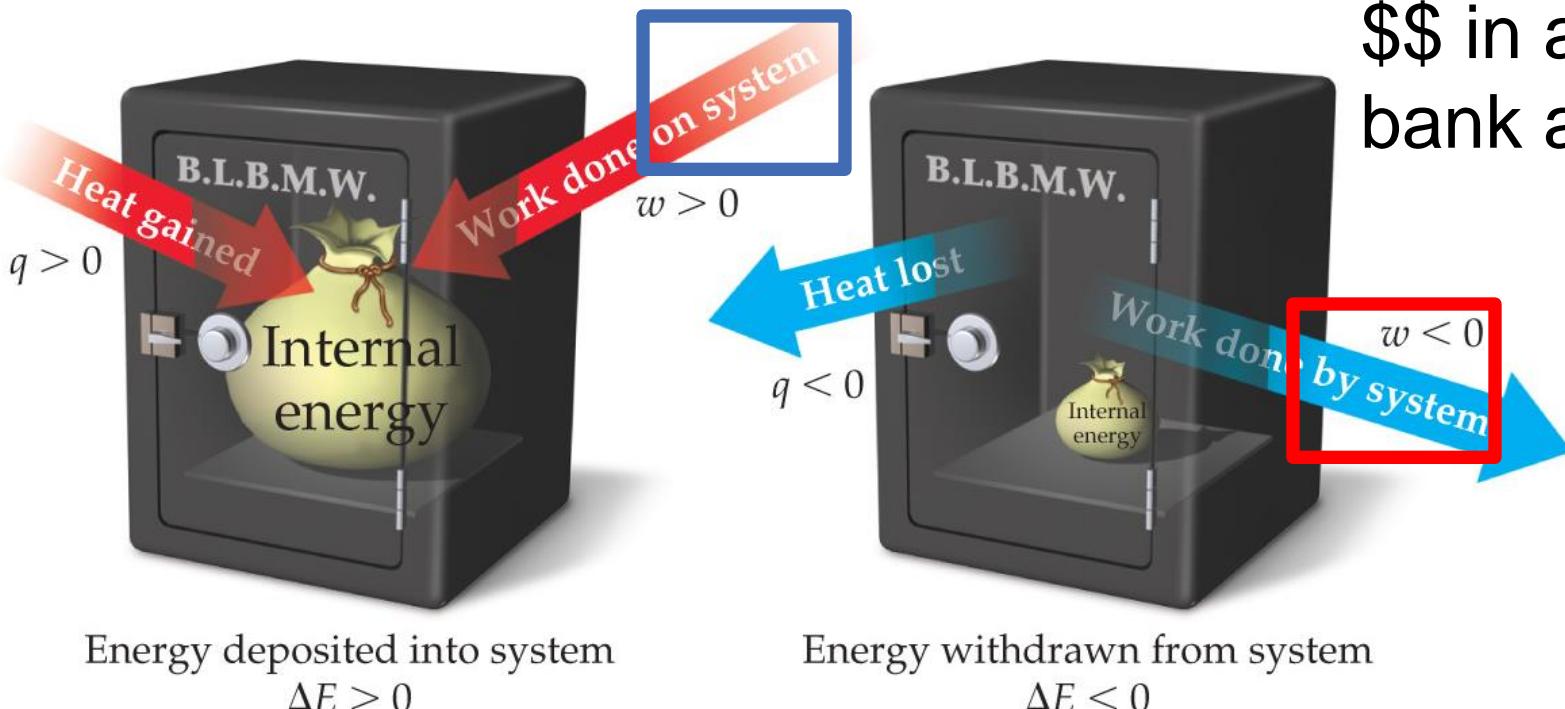
→ the **system** absorbs energy from the **surroundings**. (吸能)



When (internal) energy is **exchanged** between the **system** and the **surroundings** (First Law of Thermodynamics), it is exchanged as either **heat ( $q$ )** or **work ( $w$ )**.

$$\Delta E = q + w$$

System is interior of vault (保险库)



\$\$ in a safe or bank account

Thermochemistry

# $\Delta E$ , $q$ , $w$ , and Their Signs

TABLE 5.1 • Sign Conventions for  $q$ ,  $w$ , and  $\Delta E$

For $q$	+ means system <i>gains</i> heat	- means system <i>loses</i> heat
For $w$	+ means work done <i>on</i> system	- means work done <i>by</i> system
For $\Delta E$	+ means <i>net gain</i> of energy by system	- means <i>net loss</i> of energy by system

## Be careful:

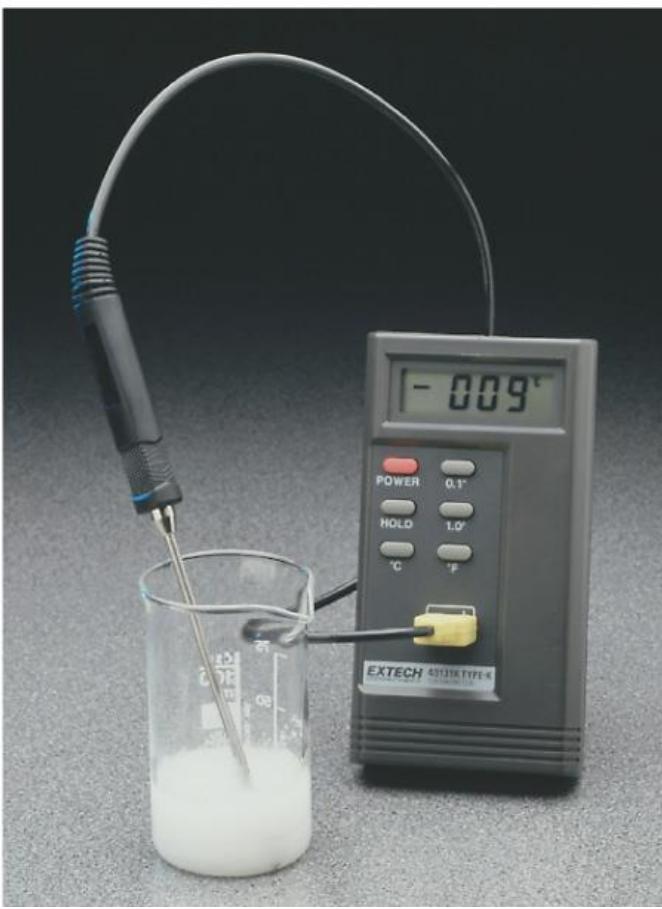
1. sign (+ or -);
2. **on** or **by** (gain or lose);
3. object (**system** or **surrounding**).



# Exchange of Heat between System and Surroundings

**System:** reactants + products

**Surroundings:** solvent,  
initially at room temperature



When **heat** is **absorbed** by the **system** ( $q > 0$ ) from the surroundings, this process is **endothermic** (吸热).

Heat flows from surroundings into system (**endothermic reaction**), temperature of surroundings drops, thermometer reads temperature well below room temperature

**System:** reactants

**Surroundings:**  
air around reactants



When **heat** is **released** by **the system** ( $q < 0$ ) into the surroundings, this process is **exothermic** (放热).

Heat flows (violently) from system into surroundings (**exothermic reaction**), temperature of surroundings increases

# Changes in Internal Energy ( $\Delta E$ )

1. If  $E_{\text{final}} > E_{\text{initial}}$ ,  $\Delta E > 0$  (+ve).

The **system** *absorbs* energy *from* the **surroundings**.

2. If  $E_{\text{final}} < E_{\text{initial}}$ ,  $\Delta E < 0$  (-ve).

The **system** *releases* energy *to* the **surroundings**.

$$\Delta E = q + w$$

## Heat Exchanges (q)

1. When **heat** is *absorbed* by the system ( $q > 0$ ) from the surroundings, the **process** is **endothermic**.

2. When **heat** is *released* by the system ( $q < 0$ ) into the surroundings, the **process** is **exothermic**.

A bowler lifts a 5.4 kg bowling ball from ground level to a height of 1.6 m and then drops it. **(a)** What happens to the **potential energy of the ball** as it is raised? **(b)** What **quantity of work**, in J, is used **to raise the ball**? **(c)** After the ball is **dropped, it gains kinetic energy**. If all the work done in part (b) has been converted to kinetic energy by the time the ball strikes the ground, what is the ball's speed just before it hits the ground? (Note: The force due to gravity is  $F = m \times g$ , where  $g = 9.8 \text{ m/s}^2$ .)

(a) Potential energy increases.

$$(b) w = F \times d = m \times g \times d = \\ (5.4 \text{ kg})(9.8 \text{ m/s}^2)(1.6 \text{ m}) = 85 \text{ kg-m}^2/\text{s}^2 = 85 \text{ J}$$

$$(c) \text{K.E} = \text{P.E. (85 J)} \quad E_k = \frac{1}{2}mv^2 = 85 \text{ J} = 85 \text{ kg-m}^2/\text{s}^2$$

chemistry

$$v = 5.6 \text{ m/s}$$

Calculate the change in the internal energy for a process in which a system absorbs 140 J of heat from the surroundings and does 85 J of work on the surroundings.

$$\begin{aligned}\Delta E &= q + w \\ &= (140 - 85) \text{ J} \\ &= -55 \text{ J}\end{aligned}$$

Work done **on** ABC: i.e. ABC **gains** energy.

Work done **by** ABC: i.e. ABC **loses** energy.



Work = \_\_\_\_\_.

- a. force x distance
- b. force / distance
- c. energy x distance
- d. energy / distance

The sum of all of the kinetic and potential energies of a system is called the

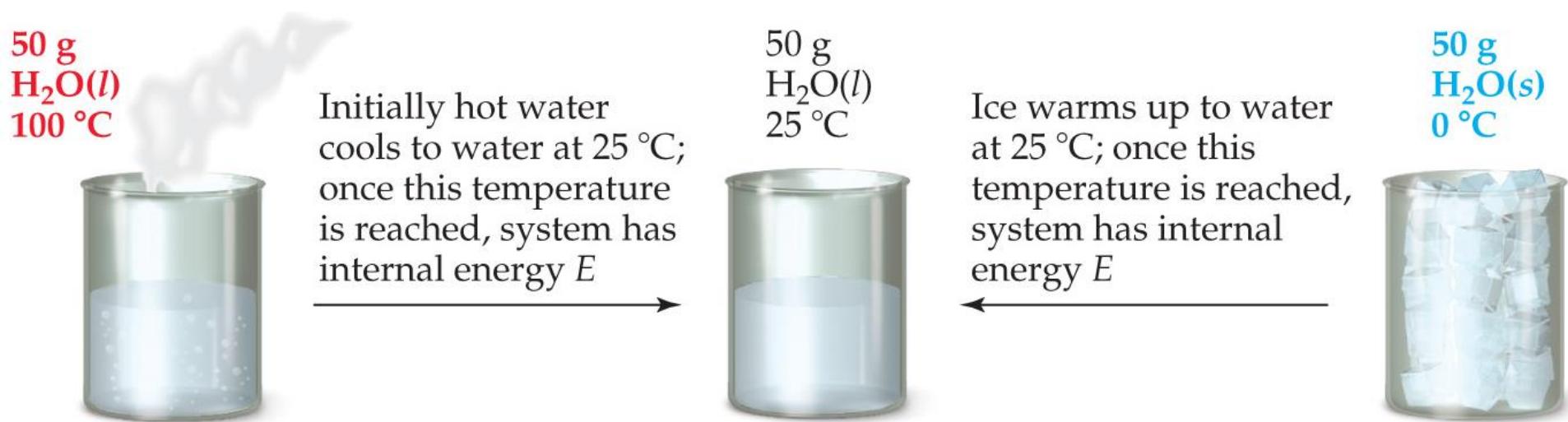
- a. integral energy.
- b. dynamic energy.
- c. internal energy.
- d. work.



# State Function (状态函数)

Usually we have **no way** of knowing the **absolute internal energy** of a system ( $E$ ); finding that value is a too complex problem.

However, we do know that the **internal energy** of a system is **independent of the path** by which the system achieved that state.



The water of the system could have reached room temperature from either direction.

**Internal energy (E)** (temperature (T), enthalpy (H), entropy (S), free energy (G), pressure (P), volume (V)...etc) is a **state function** (which describes **properties** of matter at the **equilibrium state**).

It depends only on the **present state** of the system, **not on the path/process** by which the system arrived at that state.

### By the definition of state function:

$\Delta E$  depends only on  $E_{\text{initial}}$  and  $E_{\text{final}}$ .

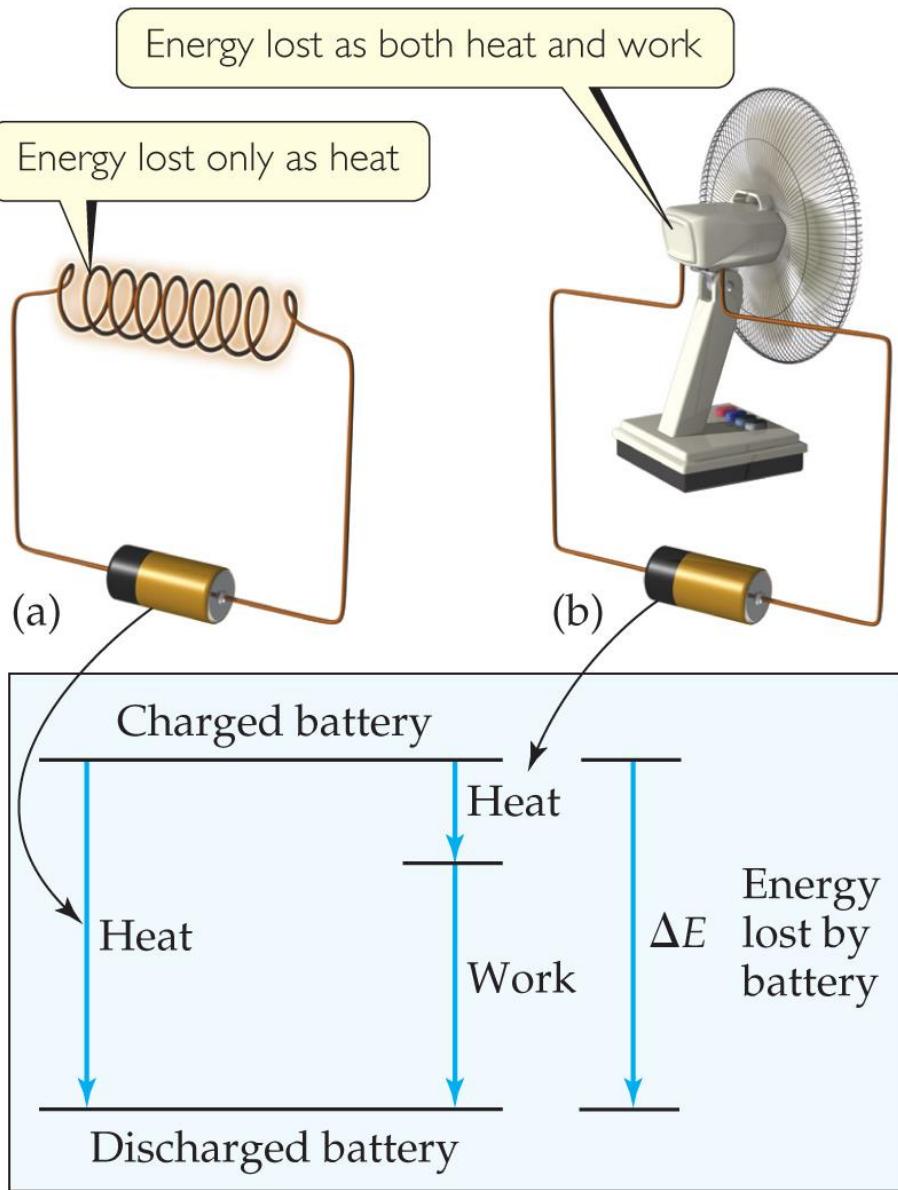


Initially hot water cools to water at 25 °C; once this temperature is reached, system has internal energy  $E$



Ice warms up to water at 25 °C; once this temperature is reached, system has internal energy  $E$





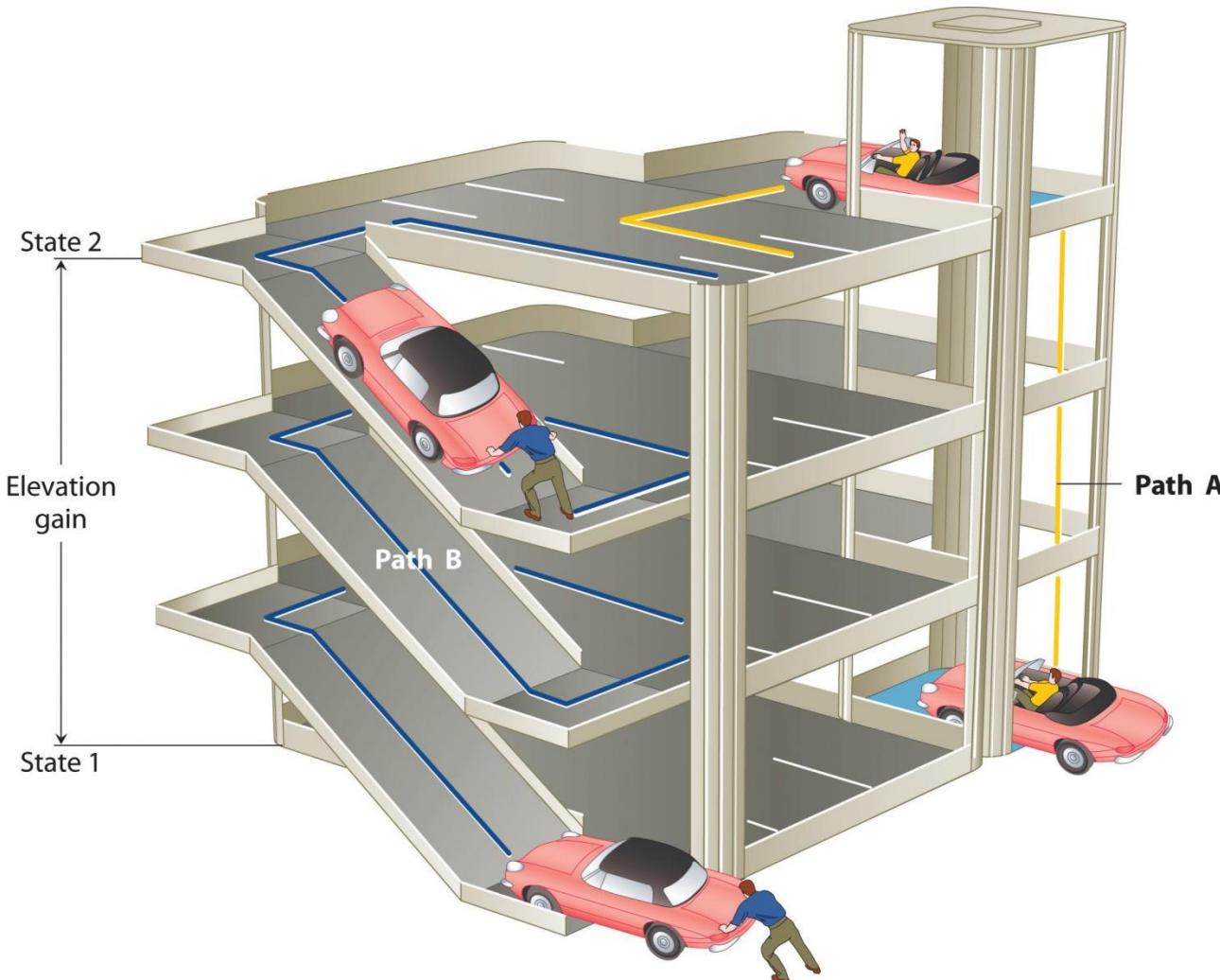
However, ***q*** and ***w*** are  
**NOT state functions.**

Whether the battery is discharged by running the fan or heater, its  $\Delta E$  is the **same**.

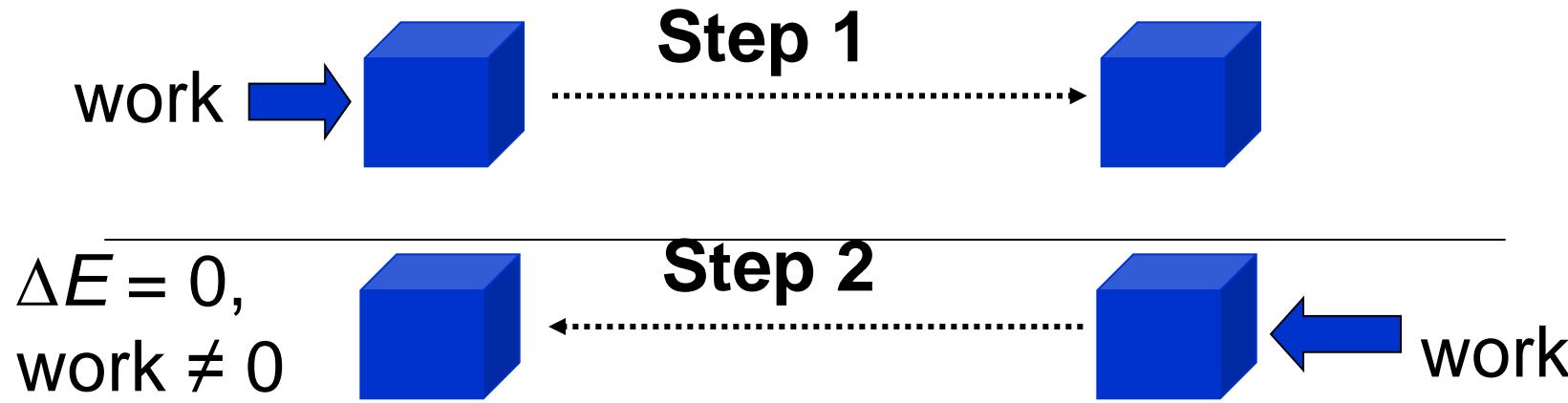
***q* & *w* are different** in the two cases:

$$\Delta E = q + w$$

A person standing on the roof of a 5 stories building has a fixed value of potential energy (P.E.), irrespective of the fact whether he reached there by stairs or lift. So, **P.E. is a state function.**



The **work** done (against friction and gravity force) to reach the same height **by lift or by stairs** is NOT same. So, **work is not a state function**. instead it is sometimes called a **path function**.



**Temperature** is a **state function** as it does not depend on the process (i.e., by heating or by cooling). **Pressure & volume** are also **state functions** because it does not depend on the process involved.

(**state function** describes **properties** of matter at the **equilibrium state**).

A system absorbs heat during an \_\_\_\_\_ process.

- a. exothermic
- b. isothermal
- c. adiabatic
- d. endothermic

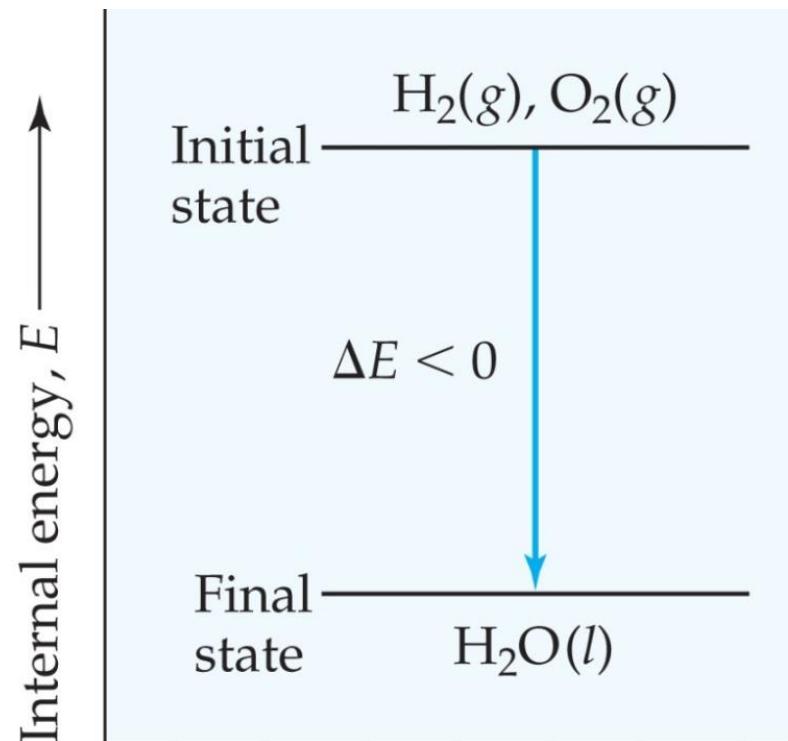
If  $X$  is a state function, then the change in  $X$  is given by  $(X_{\text{final}} - X_{\text{initial}})$ .

- a. +
- b. -
- c.  $\times$
- d.  $\div$



When  $\text{H}_2(g)$  and  $\text{O}_2(g)$  react to form  $\text{H}_2\text{O}(l)$ , heat is released to the surroundings. Consider the reverse reaction, namely, the formation of  $\text{H}_2(g)$  and  $\text{O}_2(g)$  from  $\text{H}_2\text{O}(l)$ :  $2 \text{ H}_2\text{O}(l) \longrightarrow 2 \text{ H}_2(g) + \text{O}_2(g)$ . Is this reaction exothermic or endothermic? (Hint: Refer to Figure 5.6)

- A. Endothermic, because heat is released to the surroundings.
- B. Exothermic, because heat is released to the surroundings.
- C. Endothermic, because heat is absorbed from the surroundings.
- D. Exothermic, because heat is absorbed from the surroundings.



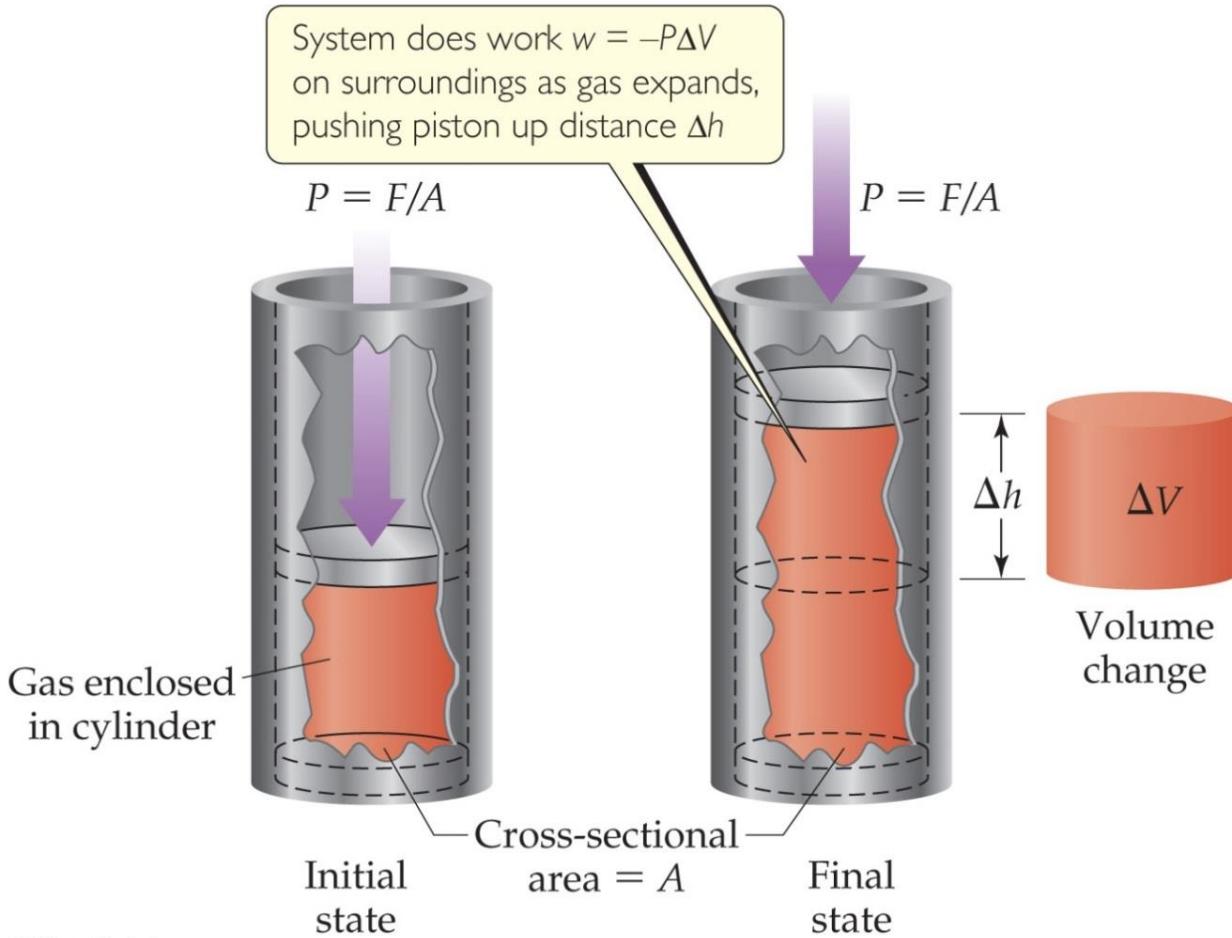
Which of these is NOT a state function?

- a. internal energy
- b. temperature
- c. enthalpy
- d. work

When a piece of iron at 356 Kelvins is placed in water at 298 Kelvins, what happens?

- a. Energy flows from iron to water.
- b. Energy flows from water to iron.
- c. Energy does not flow.
- d. Energy is not conserved.

# (Electrical or Mechanical) Work



$$\begin{aligned} w &= \text{force} * \text{distance} \\ &= -F\Delta h \text{ (work done by the system)} \\ &= -(F/A)(A\Delta h) \\ &= -(F/A)\Delta V \\ &= -P\Delta V \\ w &= -P\Delta V \end{aligned}$$

The mechanical work done by the system at **constant pressure**: expansion  $\rightarrow$  negative  $w$  value (v.s. compression  $\rightarrow$  positive  $w$  value).

# Enthalpy (焓)

**Enthalpy (H)** is the **internal energy (E)** plus the product of **pressure (P)** and **volume (V)** (**H, E, P & V are state functions**); “enthalpein” in Greek: to warm.

$$H = E + PV$$

We can account for **heat flow** during the process by measuring the **change of enthalpy ( $\Delta H$ )** of the system at **constant pressure**.

When the system changes at **constant pressure** (often against atmospheric (大气) pressure), the change in enthalpy (relative enthalpy),  $\Delta H$ :

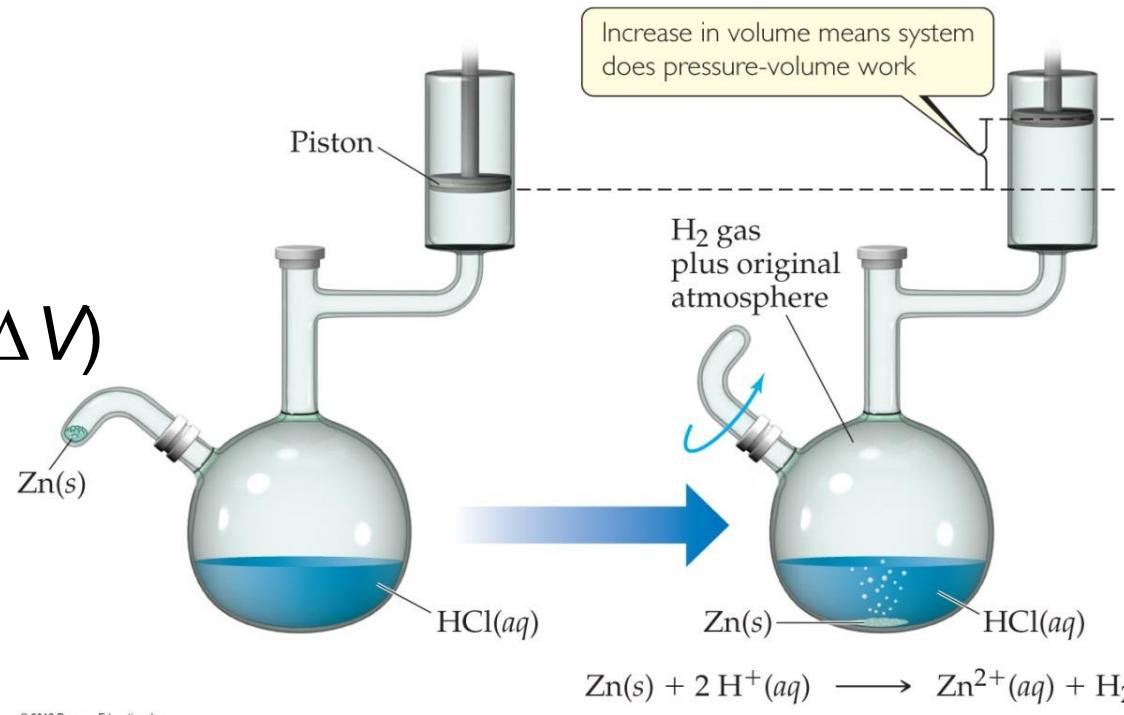
$$\Delta H = \Delta(E + PV)$$

$$\Delta H = \Delta E + P\Delta V$$

$$(\Delta E = q + w \text{ & } w = -P\Delta V)$$

$$\Delta H = (q + w) - w$$

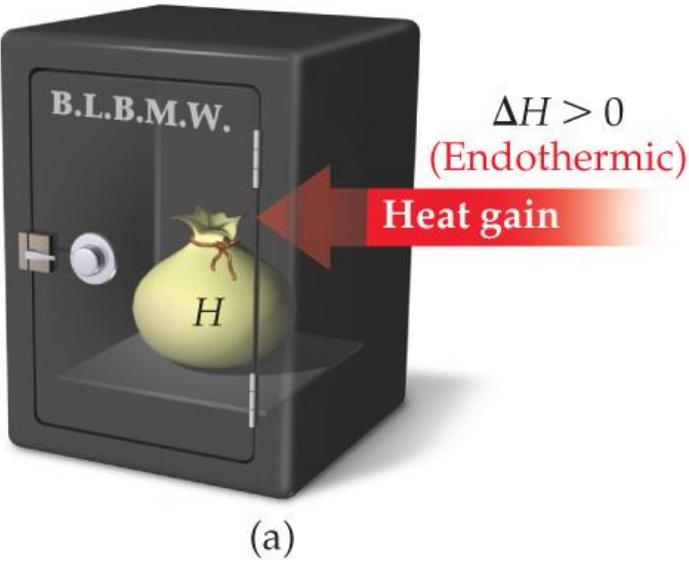
$$\Delta H = q \text{ (or } q_p\text{)}$$



**At constant pressure**,  $\Delta H$  is the **heat gained or lost only**. Heat ( $q$ ) which is experimentally measured tells us  $\Delta H$  directly and easily: **more useful** (vs.  $\Delta E$ ). Thermochemistry

# Endothermicity & Exothermicity

Constant pressure  
maintained in system



$$\Delta H = q \text{ (or } q_p\text{)}$$

- A process is **endothermic** when  $\Delta H$  is positive (**+ve**).



- A process is **exothermic** when  $\Delta H$  is negative (**-ve**).

$\Delta H$  is amount of heat that flows into or out of system under constant pressure

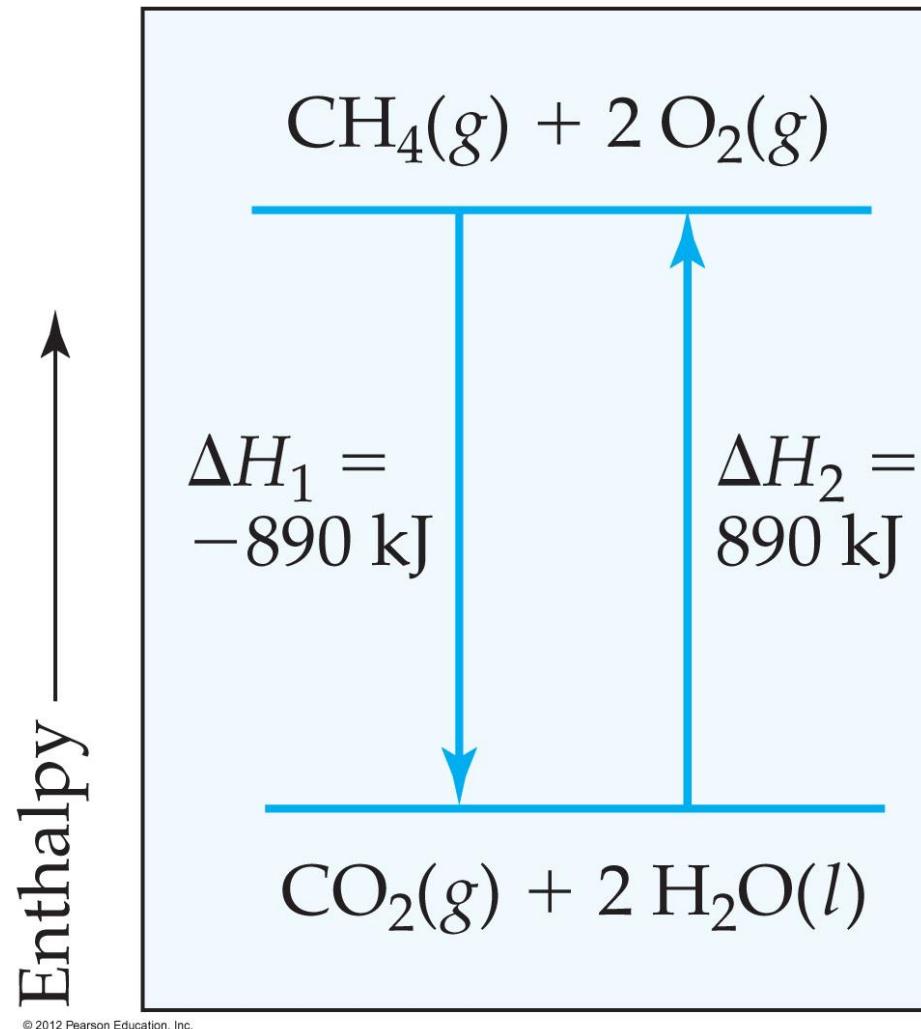
# Enthalpy of Reaction (反应焓)

The **change in enthalpy**,  $\Delta H$  (**state function**) for a reaction, is the enthalpy of the **products minus** the enthalpy of the **reactants**:

$$(\Delta H = H_{\text{final}} - H_{\text{initial}})$$

$$\Delta H = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

$$\Delta H = H(CO_2 + 2^*H_2O) - H(CH_4 + 2^*O_2)$$



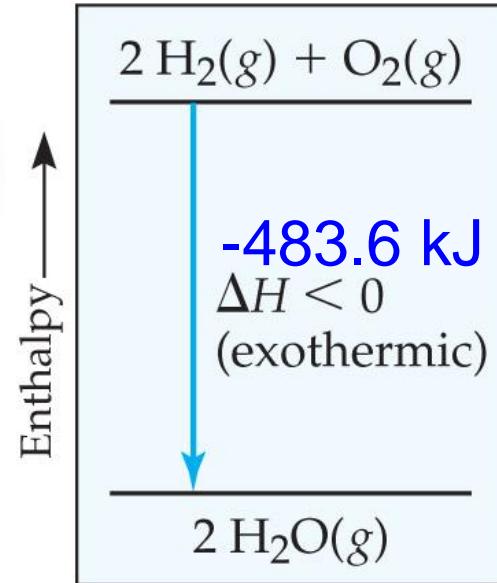
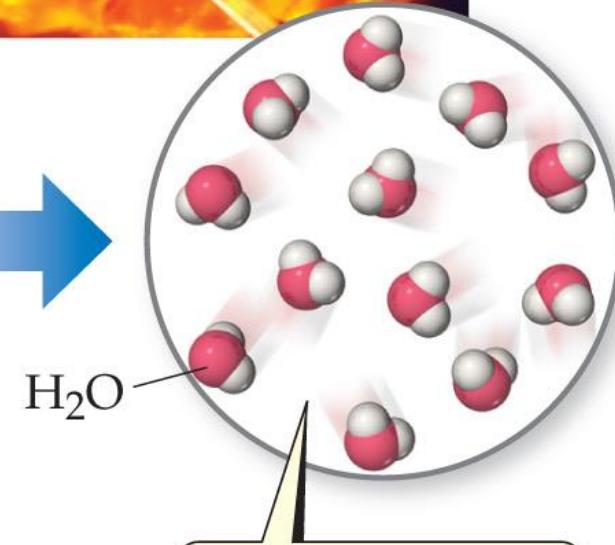
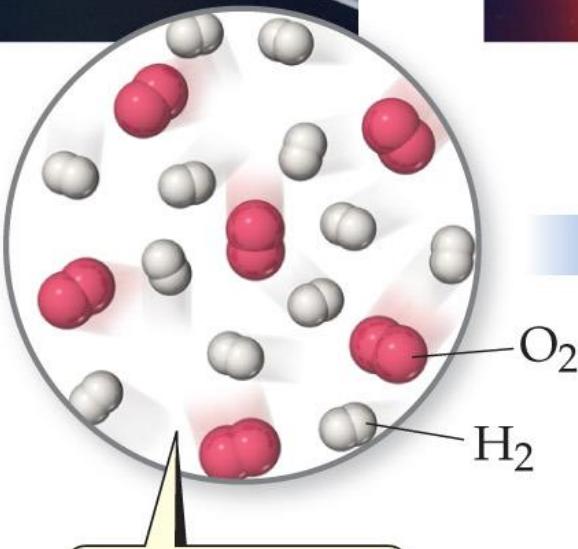
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This quantity,  $\Delta H$  ( $\Delta H_{\text{rxn}}$ ), is called the **enthalpy of reaction (rxn)**, or the **heat of reaction**.





Explosion and flame indicate system releases heat to surroundings



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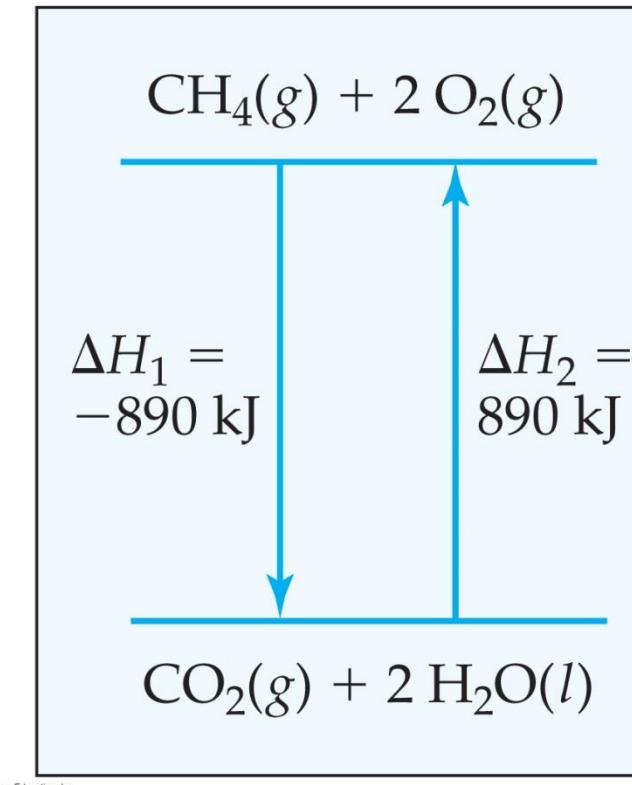
A reaction between **2 mol H<sub>2</sub>** & **1 mol O<sub>2</sub>** releases 483.6 kJ to the surroundings.

# The Truth about Enthalpy

- Enthalpy is an **extensive property**:

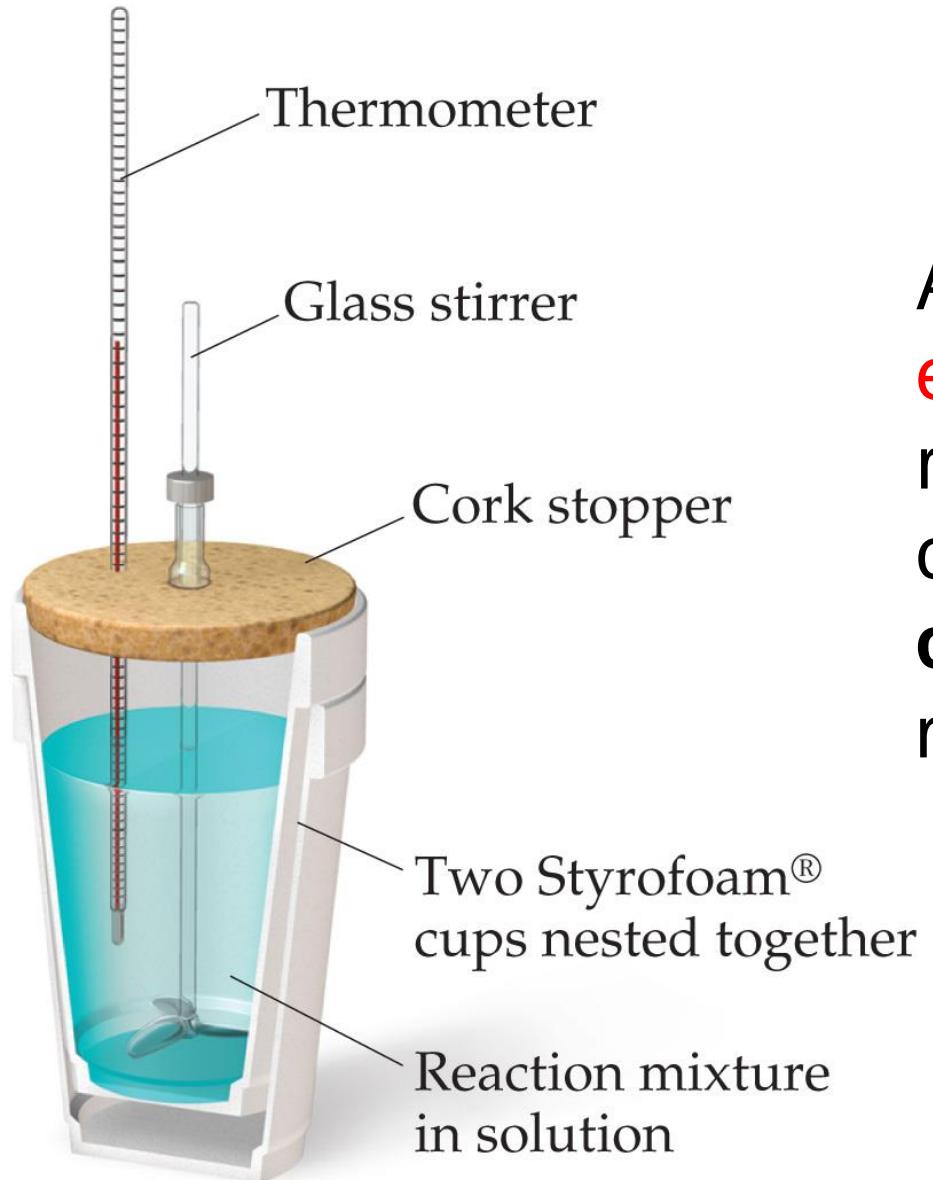
$$\begin{aligned}2 \text{ mol CH}_4 + 4 \text{ mol O}_2 &: -890^*2 \\&= -1780 \text{ kJ.}\end{aligned}$$

- $\Delta H$  for a reaction in the forward direction is **equal in size**, but **opposite in sign** to  $\Delta H$  for the **reverse** reaction (+890 kJ).



- $\Delta H$  for a reaction depends on the **state of the products** and the **state of the reactants** (-802 kJ for  $\text{H}_2\text{O}(g)$ ): **specify the states!**

# Calorimetry (量热法)



Although we **cannot** know the exact enthalpy ( $H$ ) of the reactants and products, we can **measure**  $\Delta H$  through **calorimetry**, the measurement of **heat flow**.

$$\begin{aligned}\Delta H &= H_{\text{final}} - H_{\text{initial}} \\ &= q_p\end{aligned}$$



# Heat Capacity (热容) & Specific Heat Capacity

The amount of **energy** required to **raise** the temperature of a substance by **1 K** (**1 °C**) is its **heat capacity (C)**.

$$C = \frac{\text{heat transferred}}{\text{temperature change}}$$

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

The heat capacity of 1 mole of substance: **molar heat capacity ( $C_m$ )**.

**Specific heat capacity (or specific heat,  $C_s$ ):** the amount of energy (heat  $q$ ) required to raise the temperature of **1 g of a substance** by 1 K (or 1 °C).

1.000 g H<sub>2</sub>O(*l*)  
 $T = 15.5\text{ }^\circ\text{C}$

+ 4.184 J (1 cal)  
of heat

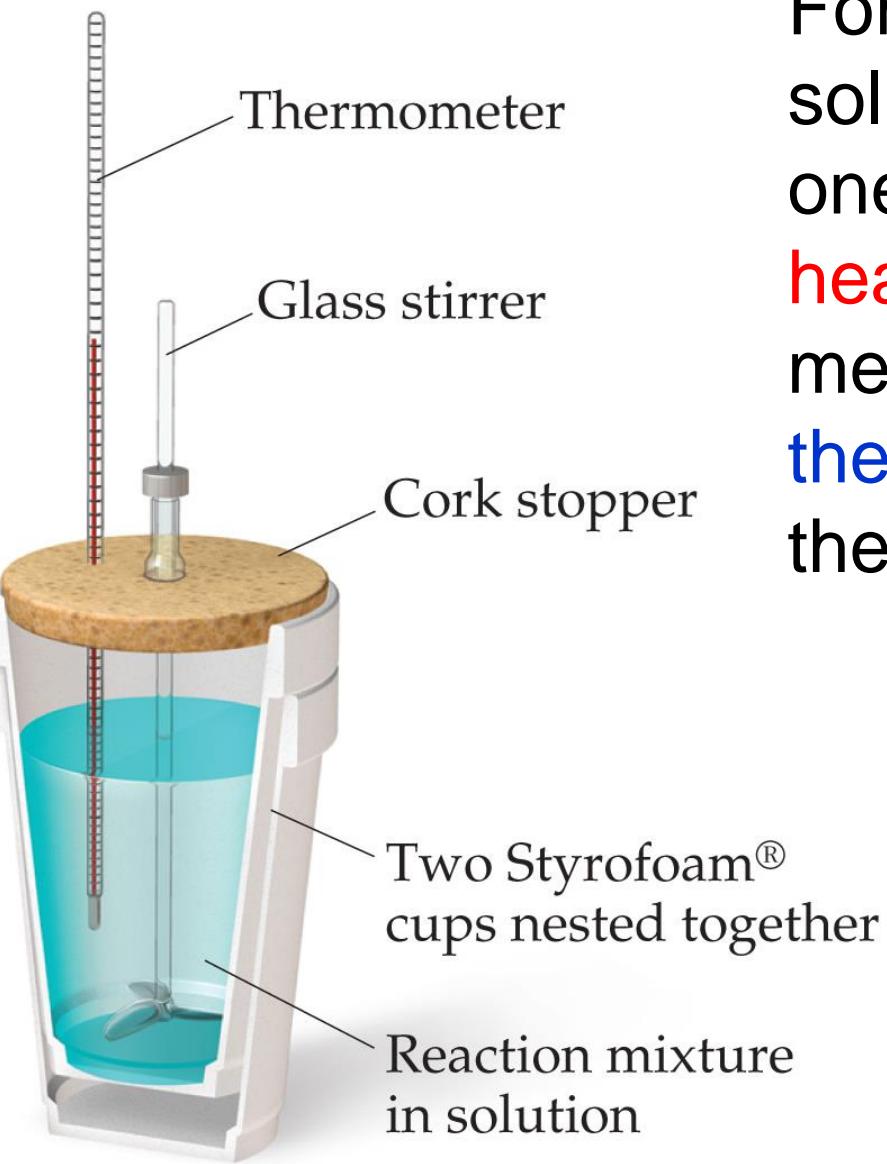
$$C_s = \frac{q}{m \times \Delta T}$$

Specific heat =  $\frac{\text{heat transferred}}{\text{mass} \times \text{temperature change}}$

**TABLE 5.2 • Specific Heats of Some Substances at 298 K**

Elements			
Substance	Specific Heat (J/g-K)	Substance	Specific Heat (J/g-K)
N <sub>2</sub> ( <i>g</i> )	1.04	H <sub>2</sub> O( <i>l</i> )	4.18
Al( <i>s</i> )	0.90	CH <sub>4</sub> ( <i>g</i> )	2.20
Fe( <i>s</i> )	0.45	CO <sub>2</sub> ( <i>g</i> )	0.84
Hg( <i>l</i> )	0.14	CaCO <sub>3</sub> ( <i>s</i> )	0.82

# Constant-Pressure Calorimetry



For a reaction in aqueous solution in a simple calorimeter, one can **indirectly measure the heat change for the system** by measuring the **heat change for the water (surrounding,  $q_{\text{soln}}$ )** in the calorimeter.

As the specific heat for water is known (4.184 J/g-K), we can measure  $\Delta H_{\text{rxn}}$  reaction:

$$q_{\text{soln}} = m \times C_s \times \Delta T$$

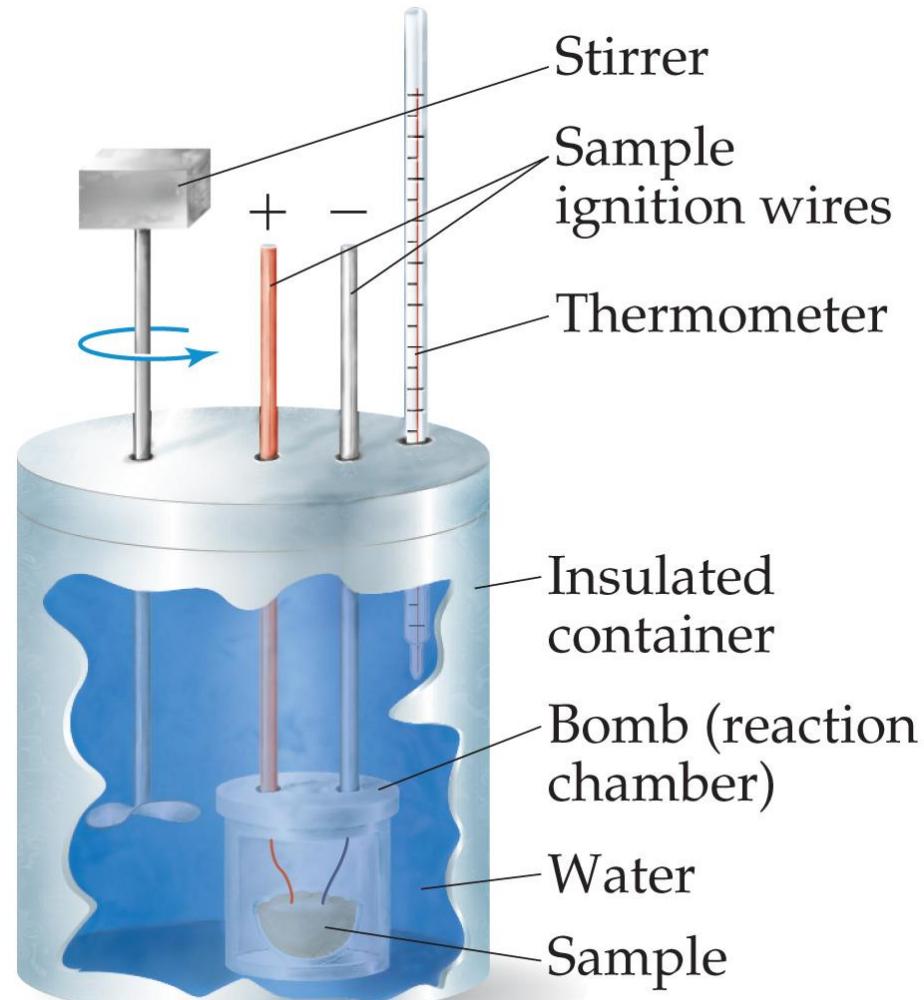
Thermochemistry

$$= -q_{\text{rxn}} = -\Delta H_{\text{rxn}}$$

# Bomb Calorimetry (弹式量热法): Constant-Volume

- Reactions can be carried out in a **sealed** (密封的) “**bomb**” (e.g. for combustion reactions with high pressure).

- As the **volume** in the bomb calorimeter is **constant**, what is measured ( $q = C^* \Delta T$ ) is the **change in internal energy**,  $\Delta E$ , NOT  $\Delta H$  (under constant P).

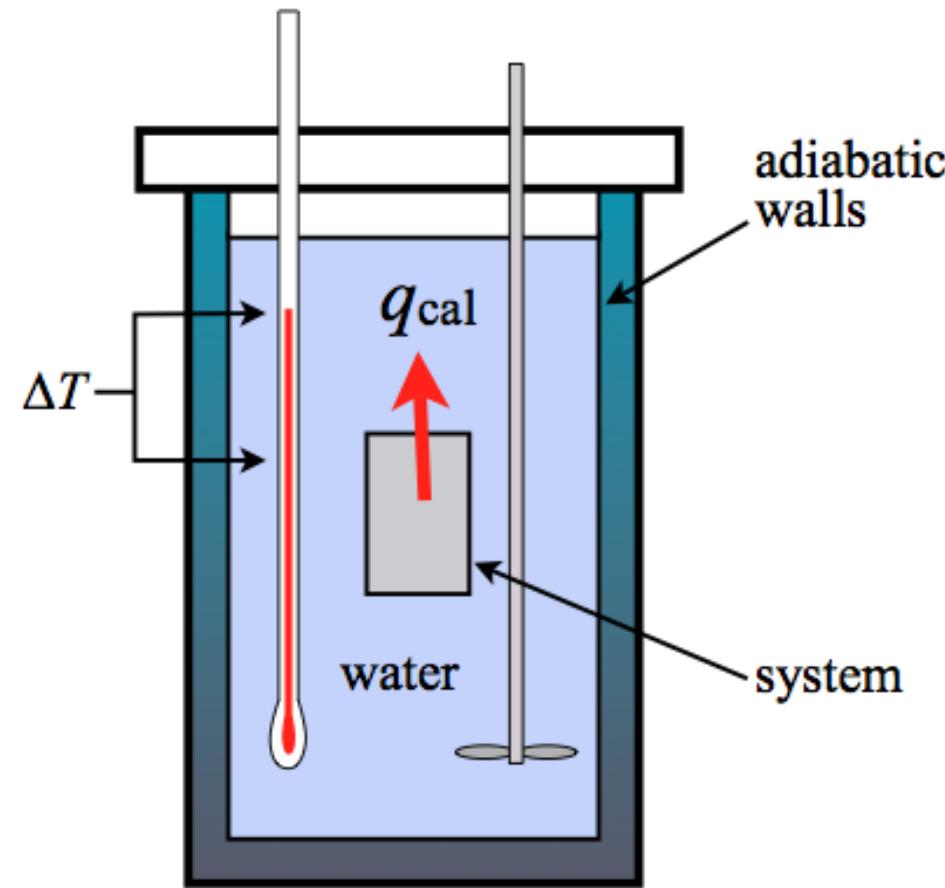


- For most reactions (e.g. in solution), the difference between  $\Delta E$  and  $\Delta H$  is very small.

$$\Delta H = \Delta(E + PV)$$

$$\Delta H = \Delta E + \Delta(PV)$$

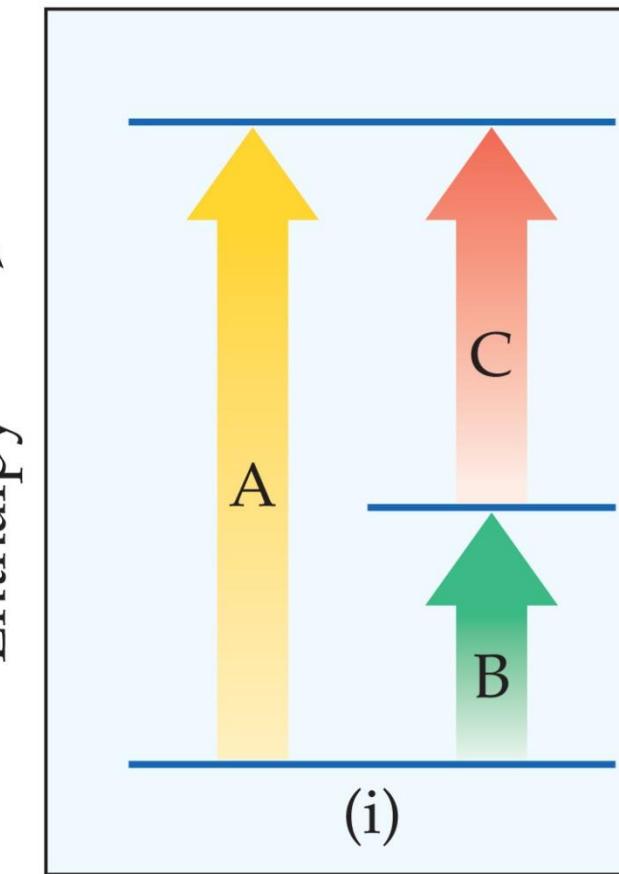
The heat absorbed (or released) by water could be a **good approximation** of the enthalpy change for the reaction (very small heat loss).



# Hess's Law

- $\Delta H_{rxn}$  is well known for many reactions, but it is not easy to measure  $\Delta H_{rxn}$  for **EVERY** reaction.
- Hess's law states: "if a reaction is carried out in **a series of steps**,  $\Delta H$  for the **overall reaction** is equal to the **sum of the enthalpy changes** for the **individual steps**".

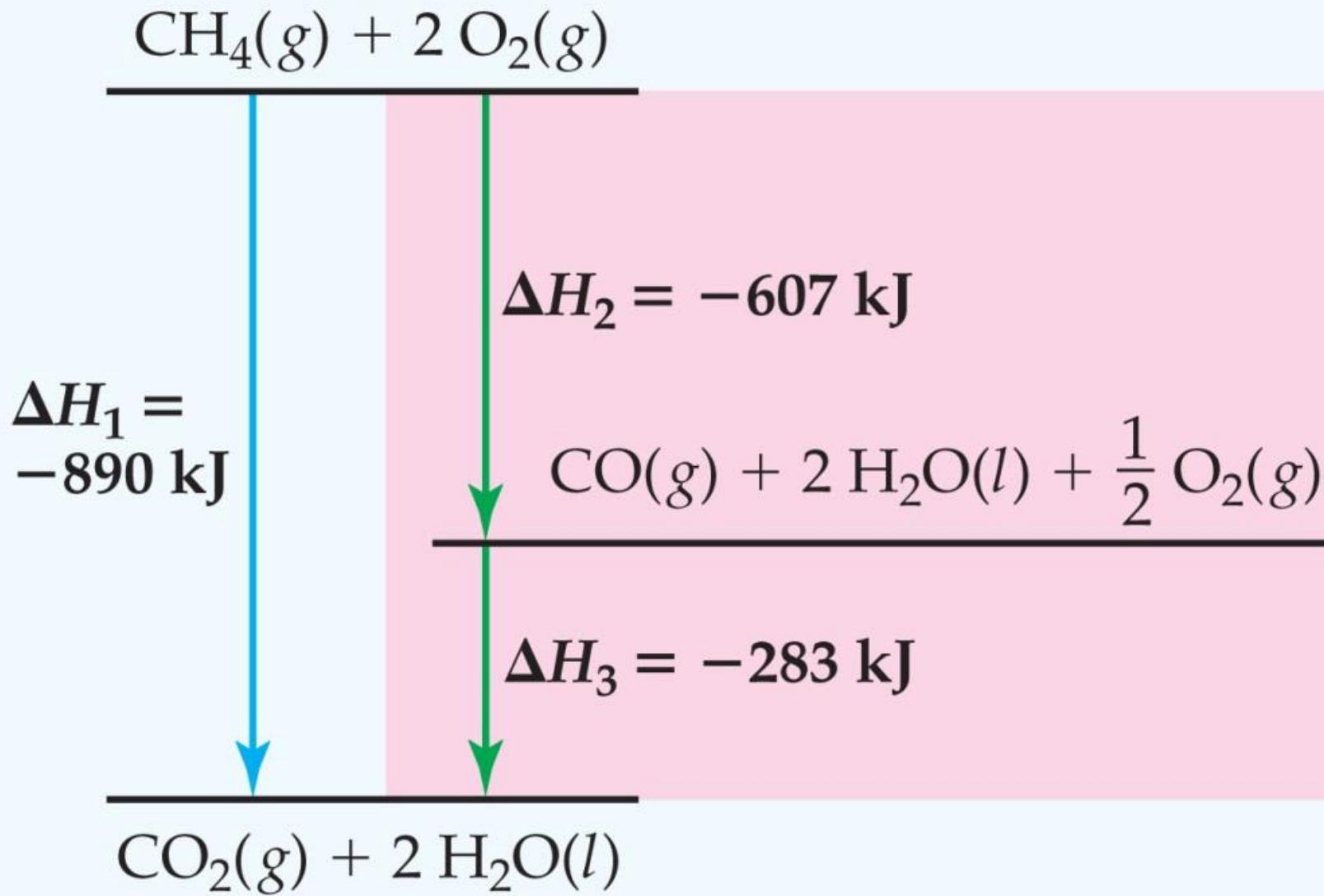
$$\Delta H_{rxn(A)} = \Delta H_{rxn(B)} + \Delta H_{rxn(C)}$$



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- As  $\Delta H$  is a **state function**, the **total enthalpy change** depends only on the **initial state** of the reactants and the **final state** of the products.

Enthalpy ↑



We can estimate  $\Delta H$  for many substances using published  $\Delta H$  values of small amounts of substances.

Thermochimistry

# Enthalpies of Formation (生成焓)

An enthalpy of formation,  $\Delta H_f$ , is defined as the **enthalpy change** for the **reaction** in which a **compound** is made **from its** (the most stable form, if more than 1 form) **elemental form** (e.g.  $H_2$ ,  $O_2$ ,  $S_8$ ).

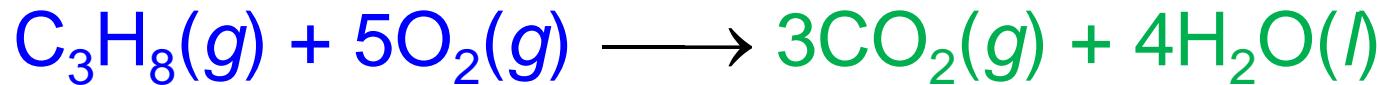
## Standard Enthalpies of Formation (标准生成焓)

Standard enthalpies of formation of a compound,  $\Delta H_f^\circ$ , are measured the enthalpy change for the **reaction to form 1 mole** of the **compound** from its **most stable elemental form** under **standard conditions** ( $25\text{ }^\circ\text{C}$  &  $1.00\text{ atm}$  pressure).

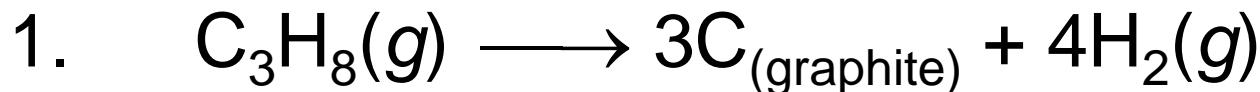
**TABLE 5.3 • Standard Enthalpies of Formation,  $\Delta H_f^\circ$ , at 298 K**

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)	Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$\text{C}_2\text{H}_2(g)$	226.7	Hydrogen chloride	$\text{HCl}(g)$	-92.30
Ammonia	$\text{NH}_3(g)$	-46.19	Hydrogen fluoride	$\text{HF}(g)$	-268.60
Benzene	$\text{C}_6\text{H}_6(l)$	49.0	Hydrogen iodide	$\text{HI}(g)$	25.9
Calcium carbonate	$\text{CaCO}_3(s)$	-1207.1	Methane	$\text{CH}_4(g)$	-74.80
Calcium oxide	$\text{CaO}(s)$	-635.5	Methanol	$\text{CH}_3\text{OH}(l)$	-238.6
Carbon dioxide	$\text{CO}_2(g)$	-393.5	Propane	$\text{C}_3\text{H}_8(g)$	-103.85
Carbon monoxide	$\text{CO}(g)$	-110.5	Silver chloride	$\text{AgCl}(s)$	-127.0
Diamond	$\text{C}(s)$	1.88	Sodium bicarbonate	$\text{NaHCO}_3(s)$	-947.7
Ethane	$\text{C}_2\text{H}_6(g)$	-84.68	Sodium carbonate	$\text{Na}_2\text{CO}_3(s)$	-1130.9
Ethanol	$\text{C}_2\text{H}_5\text{OH}(l)$	-277.7	Sodium chloride	$\text{NaCl}(s)$	-410.9
Ethylene	$\text{C}_2\text{H}_4(g)$	52.30	Sucrose	$\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)$	-2221
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6(s)$	-1273	Water	$\text{H}_2\text{O}(l)$	-285.8
Hydrogen bromide	$\text{HBr}(g)$	-36.23	Water vapor	$\text{H}_2\text{O}(g)$	-241.8

# Calculation of $\Delta H_{rxn}$ from $\Delta H_f$

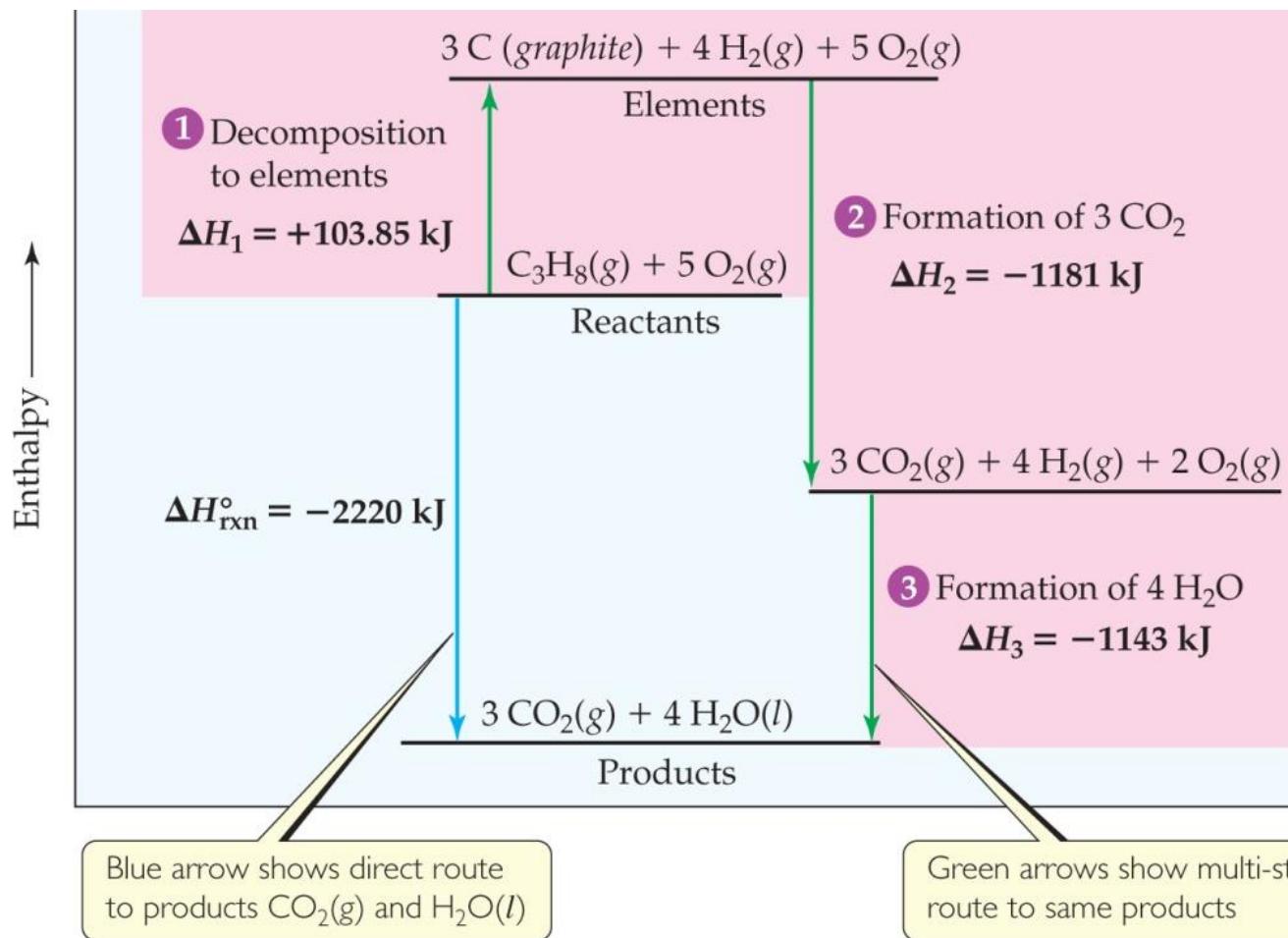
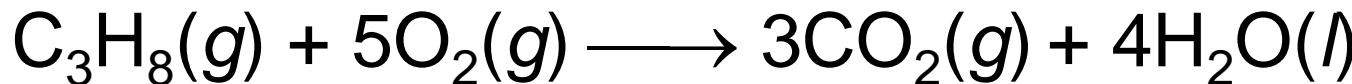


**Decomposition of the reactants** into their elemental forms ( $-\Delta H_{f,\text{reactants}}^0$ ):



**Formation of the products** from their elemental forms ( $\Delta H_{f,\text{products}}^0$ ):



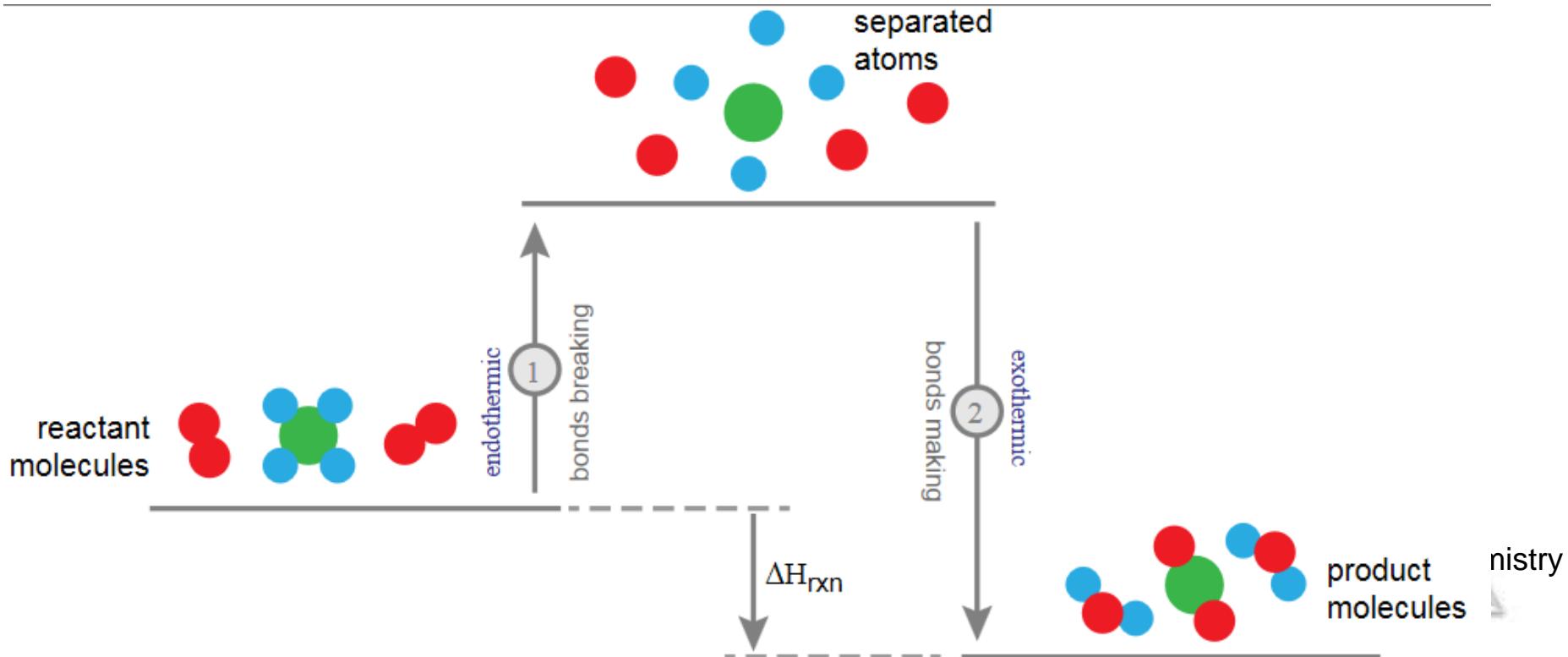


$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= \\ &\{-1^*(-103.85) - \\ &5^*(0)\} \\ &+ \{3(-393.5) + 4(- \\ &285.8)\} \\ &\approx -2220 \text{ kJ}\end{aligned}$$

We can use Hess's law in this way:

$$\Delta H_{\text{rxn}}^0 = \sum n^* \Delta H_f^0, \text{products} - \sum m^* \Delta H_f^0, \text{reactants}$$

where *n* and *m* are the stoichiometric coefficients.



If the reaction to form water were written  $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \longrightarrow \text{H}_2\text{O}(g)$ , would you expect the same value of  $\Delta H$  as in Equation 5.17? Why or why not?



Thermochemical equation

- A. Yes, because the reactants and products are the same.
- B.** No, because only half as much matter is involved.
- C. Yes, because mass does not affect enthalpy change.
- D. No, because enthalpy is a state function.



What effect do these changes have on  $\Delta H$  for a reaction:

- a. reversing the reaction,
- b. multiplying the coefficients of the equation for the reaction by 2?

a.

- A. No change.
- B. Sign of  $\Delta H$  changes.
- C. Value of  $\Delta H$  increases.
- D. Value of  $\Delta H$  decreases.

b.

- A. No change.
- B. Sign of  $\Delta H$  changes.
- C. Value of  $\Delta H$  doubles.
- D. Value of  $\Delta H$  decreases by half.



Which substance in Table 5.2 undergoes the greatest temperature change when the same mass of each substance absorbs the same quantity of heat?

- A. Hg(l)
- B. Fe(s)
- C. Al(s)
- D. H<sub>2</sub>O(l)

TABLE 5.2 • Specific Heats of Some Substances at 298 K

Elements		Compounds	
Substance	Specific Heat (J/g-K)	Substance	Specific Heat (J/g-K)
N <sub>2</sub> (g)	1.04	H <sub>2</sub> O( <i>l</i> )	4.18
Al( <i>s</i> )	0.90	CH <sub>4</sub> ( <i>g</i> )	2.20
Fe( <i>s</i> )	0.45	CO <sub>2</sub> ( <i>g</i> )	0.84
Hg( <i>l</i> )	0.14	CaCO <sub>3</sub> ( <i>s</i> )	0.82

A substance's specific heat is its heat capacity per

- a. mole.
- b. gram.
- c. joule.
- d. kelvin.

The standard enthalpy of formation of carbon in its  
**graphite** form is \_\_\_\_\_ kilojoules per mole.

- a. 100
- b. 1000
- c. 1
- d. 0



Hydrogen peroxide can decompose to water and oxygen by the following reaction:



Calculate the quantity of heat released when 5.00 g of  $\text{H}_2\text{O}_2(l)$  decomposes at constant pressure.

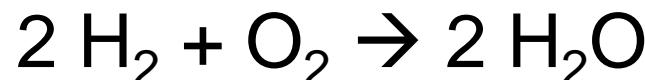
2 mol  $\text{H}_2\text{O}_2$  releases 196 kJ

Mole of  $\text{H}_2\text{O}_2 = 5.00 / (2 * 1.008 + 2 * 15.999) \text{ mol} = 0.147 \text{ mol}$

Heat(system) =  $-(0.147/2) * 196 \text{ kJ} = -14.4 \text{ kJ}$

The standard enthalpy of formation of carbon in its **diamond** form is +1.88 kJ/mole, which means that diamond is \_\_\_\_\_ graphite.

- a. as stable as
- b. more stable than
- c. less stable than
- d. an isotope of

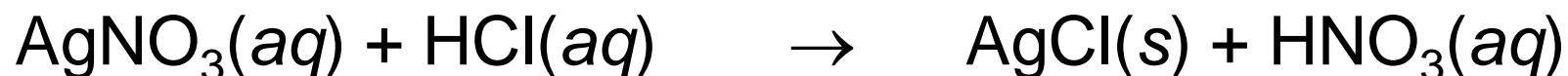


If the reaction above releases 483.6 kJ, then the standard enthalpy of formation of  $\text{H}_2\text{O}$  =

- a. -483.6 kJ/mole.
- b. +483.6 kJ/mole.
- c. -241.8 kJ/mole.
- d. +241.8 kJ/mole.



When 50.0 mL of 0.100 M  $\text{AgNO}_3$  and 50.0 mL of 0.100 M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30 °C to 23.11 °C. The temperature increase is caused by the following reaction:



Calculate  $\Delta H$  for this reaction in  $\text{AgNO}_3$ , assuming that the combined solution has a mass of 100.0 g and a specific heat of 4.18 J/g °C.

$$\text{Mole of } \text{AgNO}_3 = 0.05 * 0.100 \text{ mol} = 0.00500 \text{ mol}$$

$$\Delta T = 23.11 - 22.30 \text{ } ^\circ\text{C} = 0.81 \text{ } ^\circ\text{C}$$

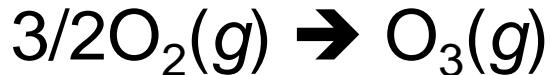
$$\text{Enthalpy} = \text{Heat} = -4.18 * 100.0 * 0.81 \text{ J} = -338.58 \text{ J} = -340 \text{ J}$$

→

$$-338.58 / 0.00500 \text{ J/mol} = -67716 \text{ J/mol} = -68 \text{ kJ/mol}$$



Calculate  $\Delta H$  for the reaction



$$\Delta H = -198.9 - (-142.3) - \textcolor{blue}{0.5} * (495.0) \text{ kJ} = -304.1 \text{ kJ}$$



The combustion of  $\text{CH}_6\text{N}_2$  produces  $\text{N}_2(g)$ ,  $\text{CO}_2(g)$  &  $\text{H}_2\text{O}(l)$ :

$$2 \text{CH}_6\text{N}_2(l) + 5 \text{O}_2(g) \rightarrow 2 \text{N}_2(g) + 2 \text{CO}_2(g) + 6 \text{H}_2\text{O}(l)$$

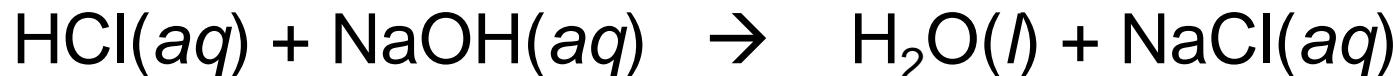
When 4.00 g of  $\text{CH}_6\text{N}_2$  is combusted in a bomb calorimeter, the temperature of the calorimeter increases from 25.00 °C to 39.50 °C. The heat capacity of the calorimeter is measured to be 7.794 kJ/ °C. Calculate the heat of reaction for the combustion of a mole of  $\text{CH}_6\text{N}_2$ .

$$\begin{aligned}\text{Mole of } \text{CH}_6\text{N}_2: 4.00 / (12.011 + 6 \cdot 1.008 + 2 \cdot 14.007) \text{ mol} \\ = 0.0868 \text{ mol}\end{aligned}$$

$$\Delta T = 39.50 - 25.00 \text{ } ^\circ\text{C} = 14.50 \text{ } ^\circ\text{C}$$

$$\begin{aligned}\Delta H = q &= -7.794 \cdot 14.50 \text{ kJ} = -113.0 \text{ kJ} \\ &= -113.0 / 0.0868 \text{ kJ/mol} = -1301.84 \text{ kJ/mol} \\ &= -1.30 \cdot 10^3 \text{ kJ/mol}\end{aligned}$$

When a student mixes 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0 °C to 27.5 °C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the total volume of the solution is 100 mL, its density is 1.0 g/mL, & its specific heat is 4.18 J/g–K.



Mass of the solution:  $100 \text{ mL} * 1.0 \text{ g/mL} = 100 \text{ g}$

Mole of HCl:  $0.050 * 1.0 \text{ mol} = 0.050 \text{ mol}$

$$\Delta T = 27.5 - 21.0 \text{ } ^\circ\text{C} = 6.5 \text{ } ^\circ\text{C} = 6.5 \text{ K}$$

$$\begin{aligned}\Delta H = q &= -4.18 * 100 * 6.5 \text{ J} = -2717 \text{ J} = -3 \text{ kJ} \\ \rightarrow -3 / 0.050 \text{ kJ/mol} &= -60 \text{ kJ/mol}\end{aligned}$$



Ozone,  $\text{O}_3(g)$ , is a form of elemental oxygen produced during electrical discharge. Is  $\Delta H_f^\circ$  for  $\text{O}_3(g)$  necessarily zero?

- A. Yes, because it is just another elemental form of oxygen.
- B. No, because it is not the most stable form of the element oxygen at the given conditions.
- C. Yes, because changing the subscripts of an elemental formula does not change standard heat of formation.
- D. No, because there is a temperature change when ozone is formed.



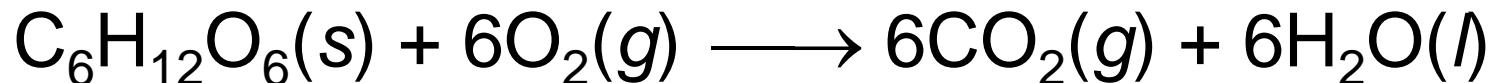
# Energy in Foods

Most of the fuel in food we eat comes from carbohydrates (碳水化物) & proteins (蛋白质) (17 kJ/g) & fats (脂肪) (38 kJ/g): our bodies stores excess as fats.

TABLE 5.4 • Compositions and Fuel Values of Some Common Foods

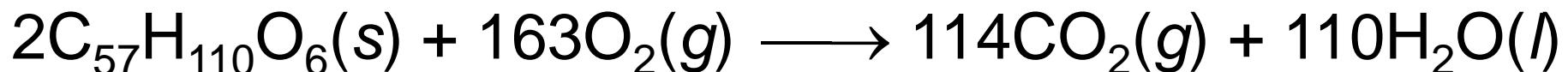
	Approximate Composition (% by mass)			Fuel Value	
	Carbohydrate	Fat	Protein	kJ/g	kcal/g (Cal/g)
Carbohydrate	100	—	—	17	4
Fat	—	100	—	38	9
Protein	—	—	100	17	4
Apples	13	0.5	0.4	2.5	0.59
Beer <sup>†</sup>	1.2	—	0.3	1.8	0.42
Bread	52	3	9	12	2.8
Cheese	4	37	28	20	4.7
Eggs	0.7	10	13	6.0	1.4
Fudge	81	11	2	18	4.4
Green beans	7.0	—	1.9	1.5	0.38
Hamburger	—	30	22	15	3.6
Milk (whole)	5.0	4.0	3.3	3.0	0.74
Peanuts	22	39	26	23	5.5

Glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$  葡萄糖/血糖)



$$\Delta H^0 = -2,803 \text{ kJ}$$

Tristearin ( $\text{C}_{57}\text{H}_{110}\text{O}_6$  三硬脂酸甘油脂)



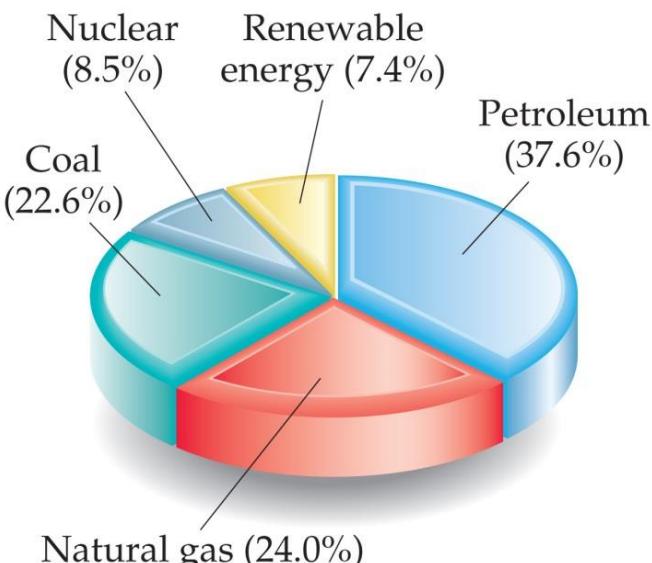
$$\Delta H^0 = -75,520 \text{ kJ}$$



# Energy in Fuels

TABLE 5.5 • Fuel Values and Compositions of Some Common Fuels

	Approximate Elemental Composition (mass %)			Fuel Value (kJ/g)
	C	H	O	
Wood (pine)	50	6	44	18
Anthracite coal (Pennsylvania)	82	1	2	31
Bituminous coal (Pennsylvania)	77	5	7	32
Charcoal	100	0	0	34
Crude oil (Texas)	85	12	0	45
Gasoline	85	15	0	48
Natural gas	70	23	0	49
Hydrogen	0	100	0	142



The vast majority of the energy consumed in USA comes from fossil (化石) fuels (petroleum 石油, natural gas 天然气 & coal 煤) → CO<sub>2</sub> & SO<sub>2</sub>

Non-renewable energy

Thermochemistry

**Renewable** (可再生的) **Energy Sources:**  
**Solar** energy (太阳能) from Sun;  
**Wind** (风) energy;  
**Geothermal** (地热) energy from heat inside the earth;

**Hydroelectric** (水力发电) energy from rivers;  
**Biomass** (生物量) energy from crops and biological waste matter.

*Hydroelectric energy & Biomass energy* are major sources in USA

**Other clean energy:**

**Hydrogen fuel** (storage)  $-483.6\text{ kJ}$   
 $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(g)$

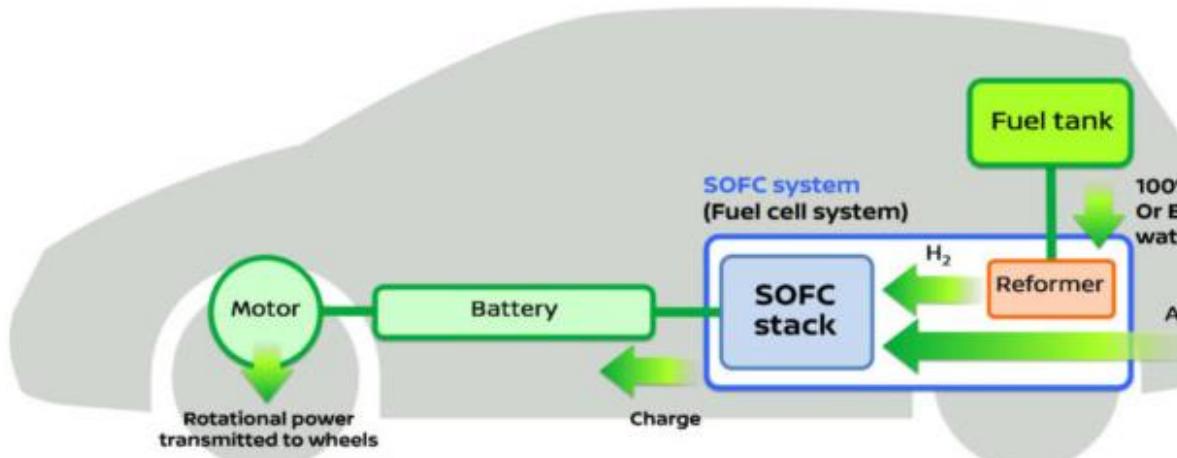
Mirai (Toyota)



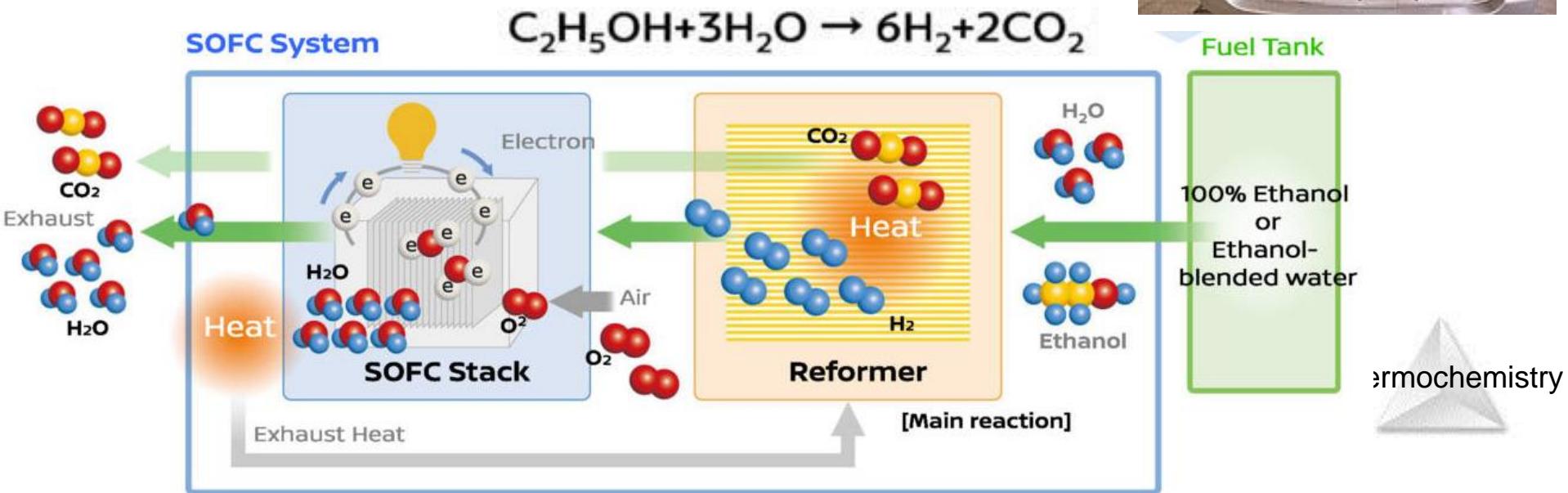
**Efficiency, costs & environment**

## How the e-Bio Fuel Cell system works 1/2

- Fueled by liquid fuel: easy to handle, can use conventional fuel tank
- Hydrogen generated through reformation of 100% ethanol or ethanol-blended water
- Power generated by SOFC (solid oxide fuel cell) stack from reformate hydrogen and air
- Generated electricity charges battery and powers drive motor



## (Extra Info.) Reforming ethanol (or methanol)



Which releases the greatest amount of energy per gram when metabolized:  
carbohydrates, proteins, or fats?

- A. Carbohydrates
- B. Proteins
- C. Fats

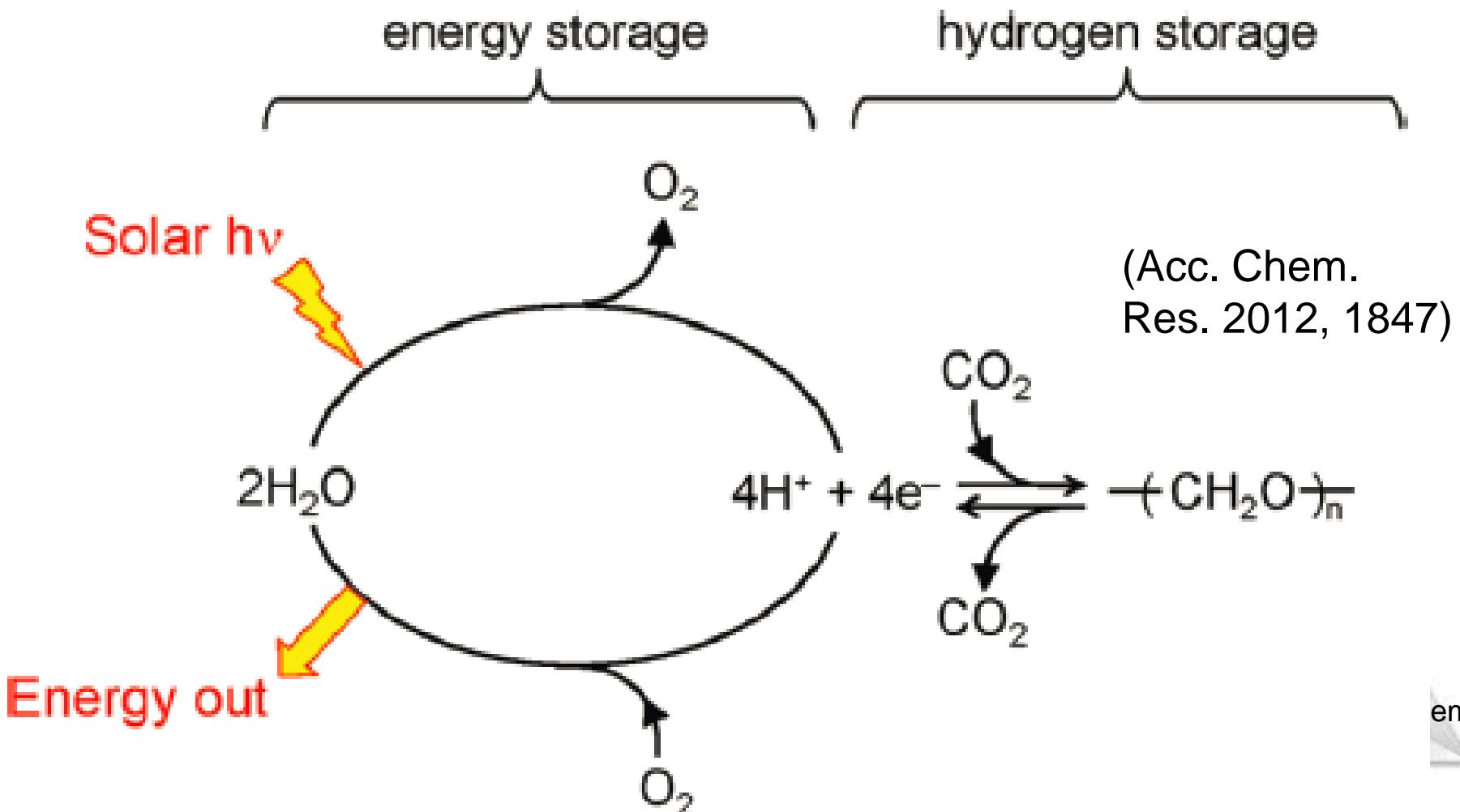
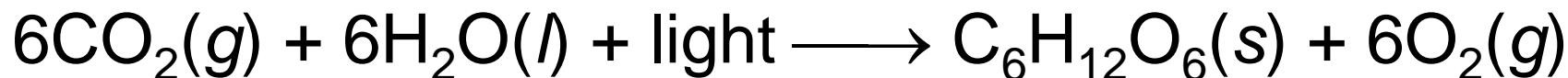
Which of these is NOT a renewable form of energy?

- a. nuclear energy
- b. solar energy
- c. geothermal energy
- d. hydroelectric energy

Much current research is directed toward using hydrogen gas,  $H_2(g)$ , as a fuel. What intrinsic advantage does hydrogen as a fuel have with respect to the current climate-change debate?

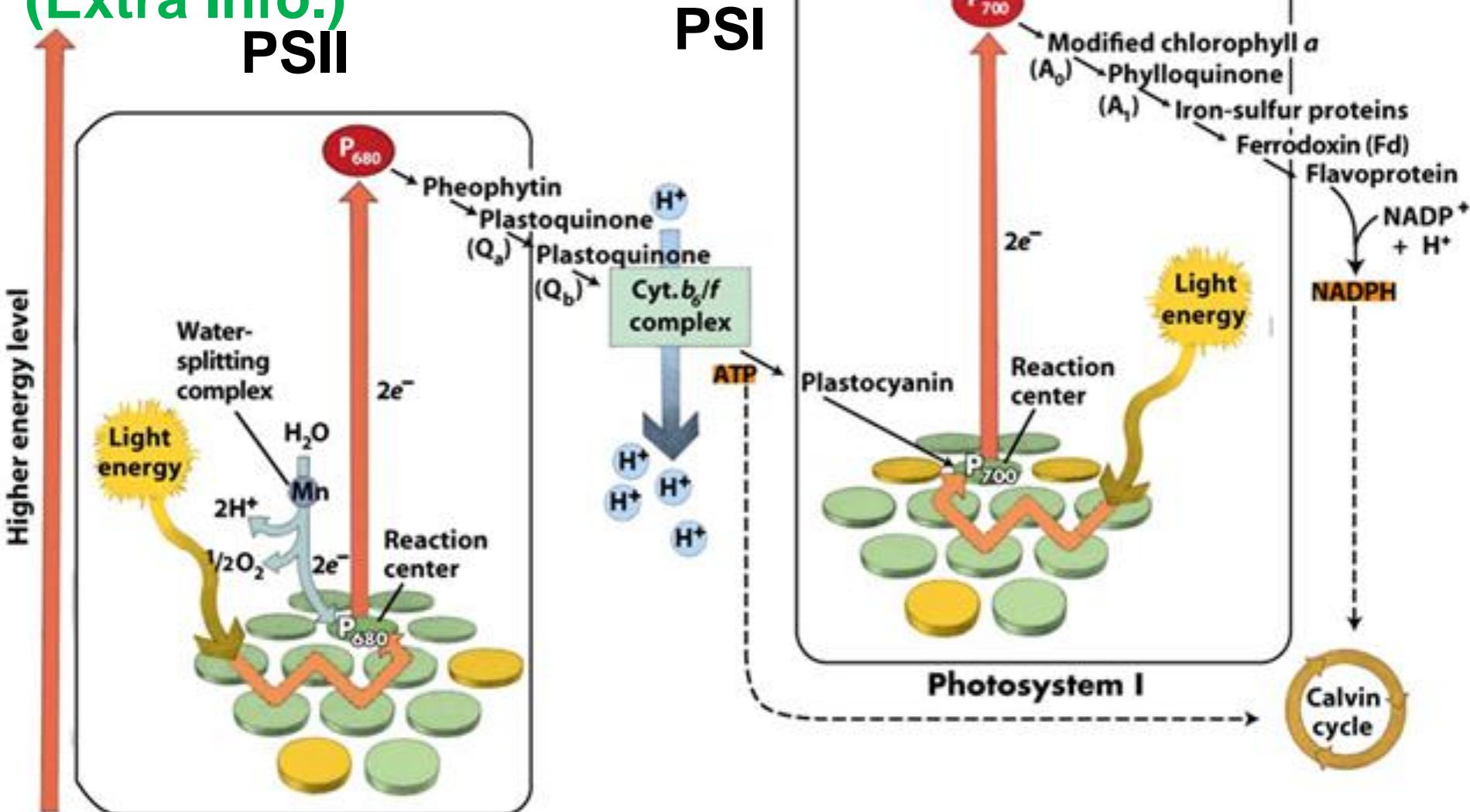
- A. It is easily stored as a gas for a long time.
- B. Its product of combustion is only  $H_2O(g)$ .
- C. Safety considerations using hydrogen gas are minimal.
- D. It is easily found in nature as an element.

# (Extra Info.) Photosynthesis (光合作用). Essay?



# (Extra Info.)

## PSII



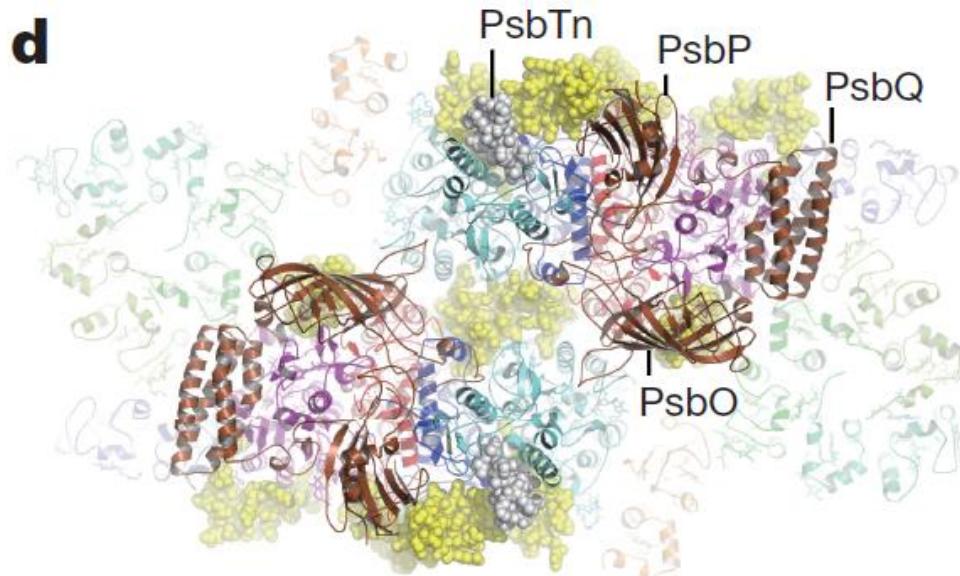
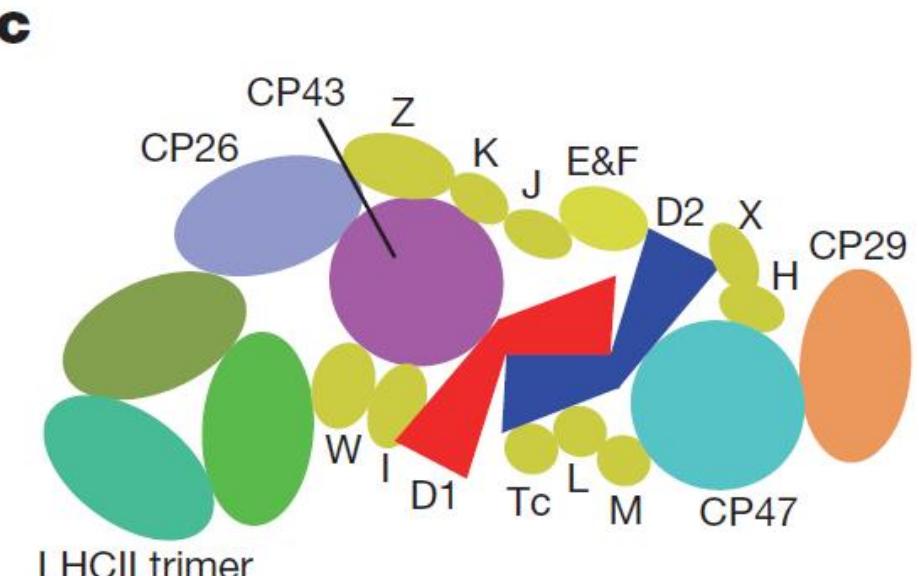
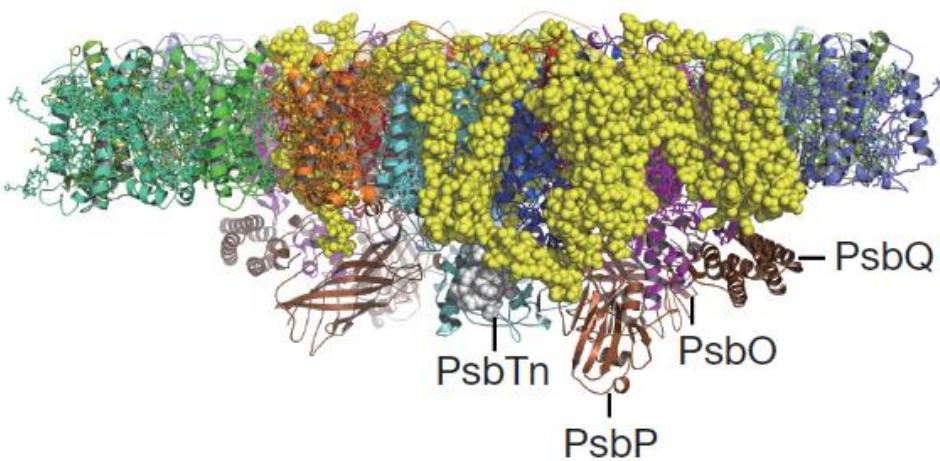
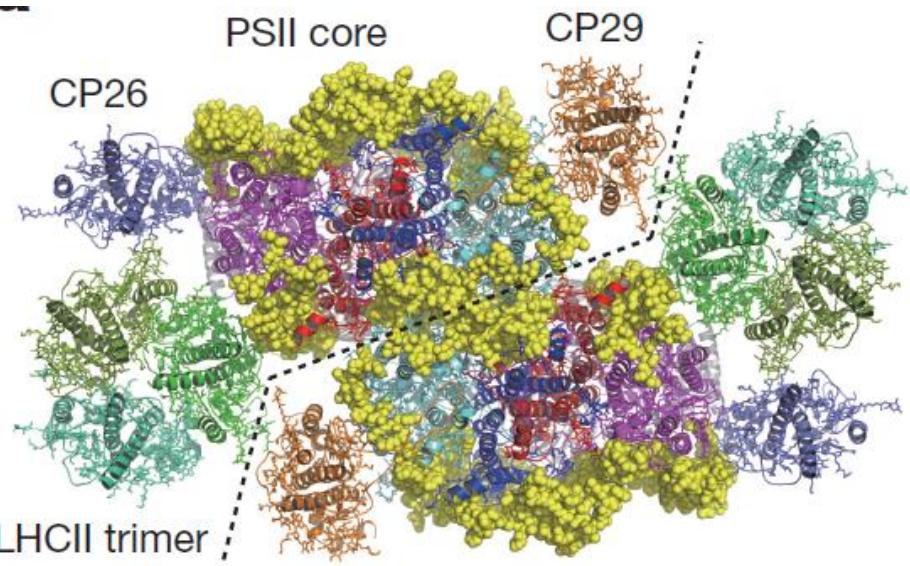
The sequence of  $e^-$  carriers in oxygenic photosynthesis

$H_2O \rightarrow$  PSII  $\rightarrow$  plastoquinone  $\rightarrow$  cytochrome  $b_6f$

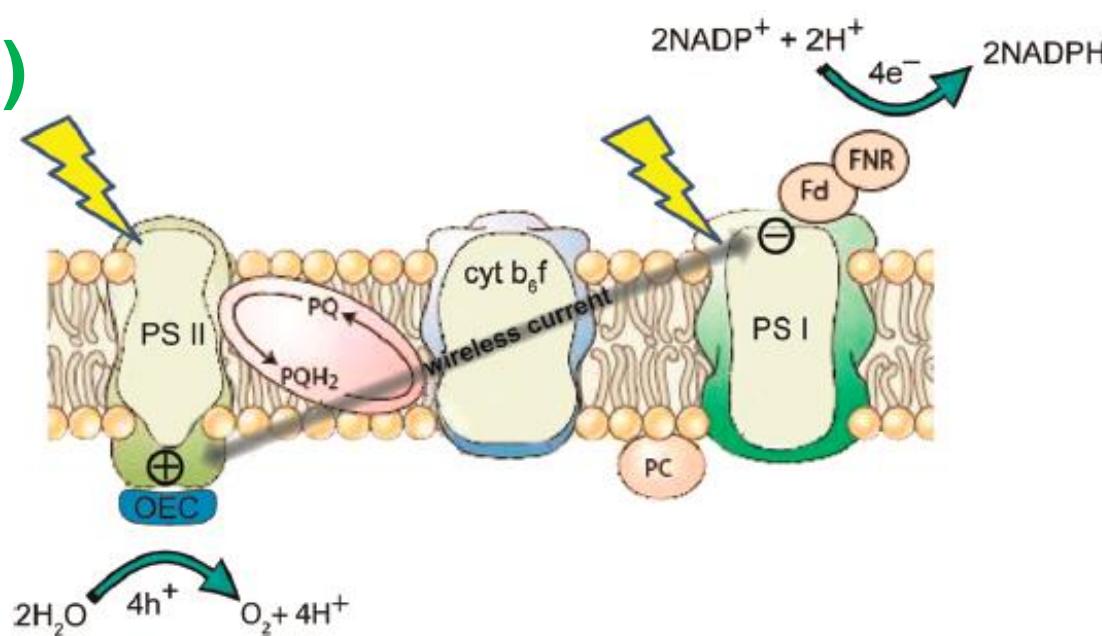
istry

$\rightarrow$  plastocyanin  $\rightarrow$  PSI  $\rightarrow$  ferredoxin  $\rightarrow$  NADP

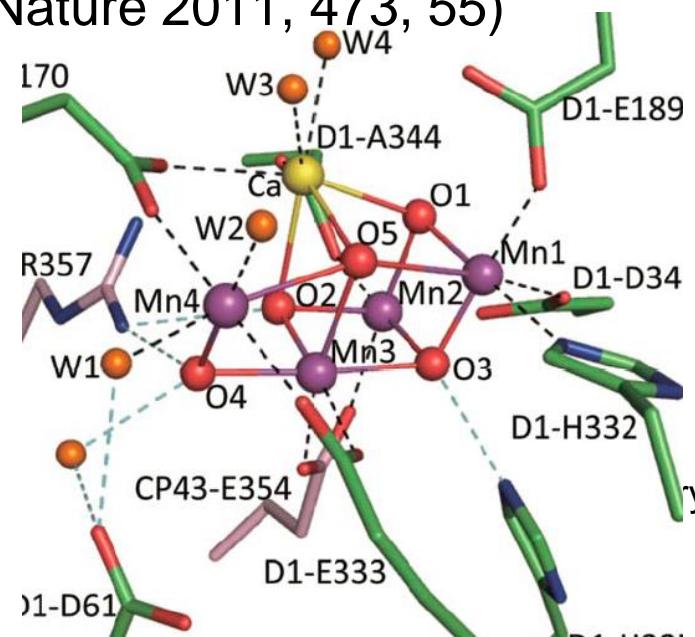
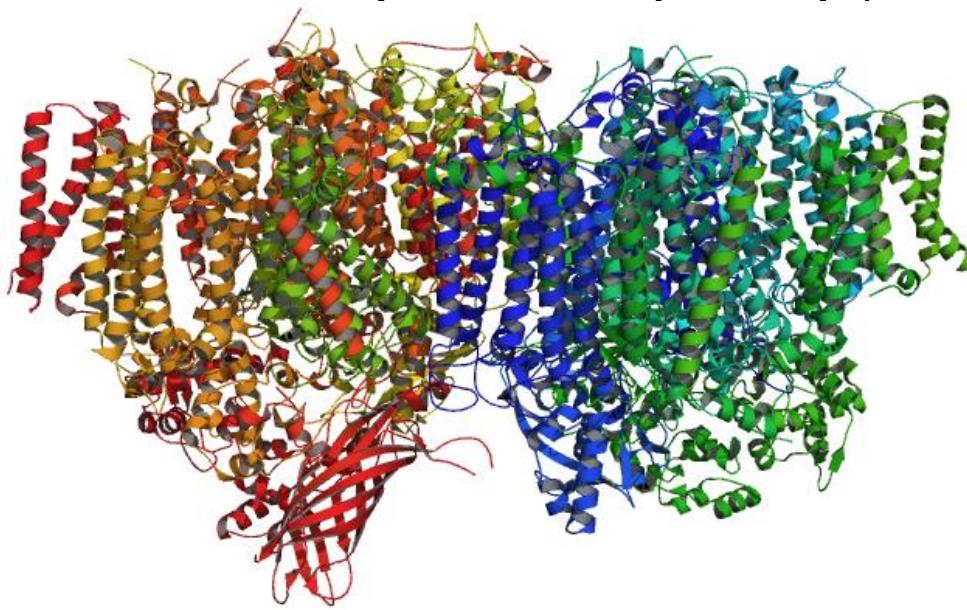
# Crystal Structure of PS II-LHC II Supercomplex (3.2Å) (Extra Info.)



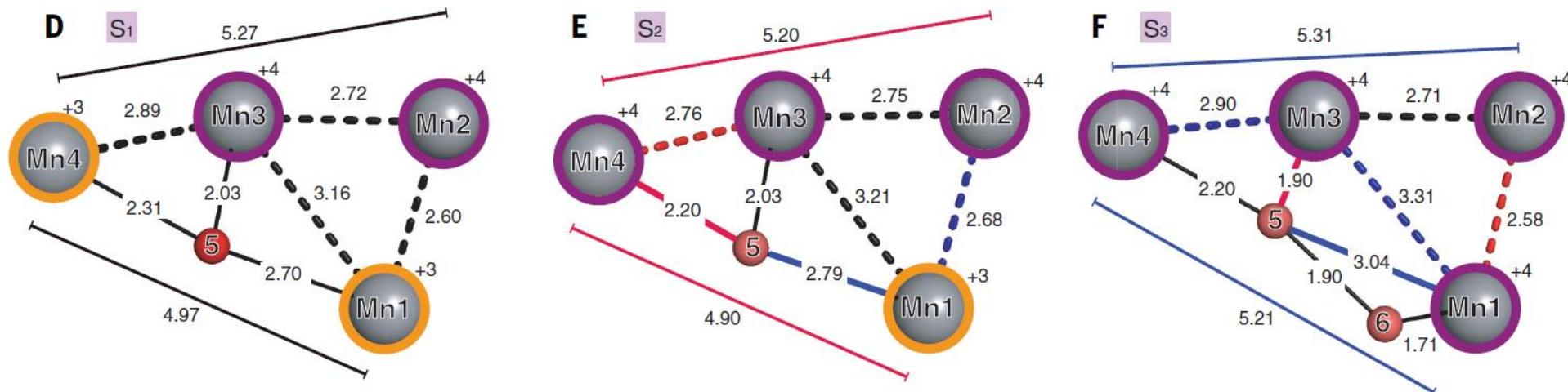
(Extra Info.)



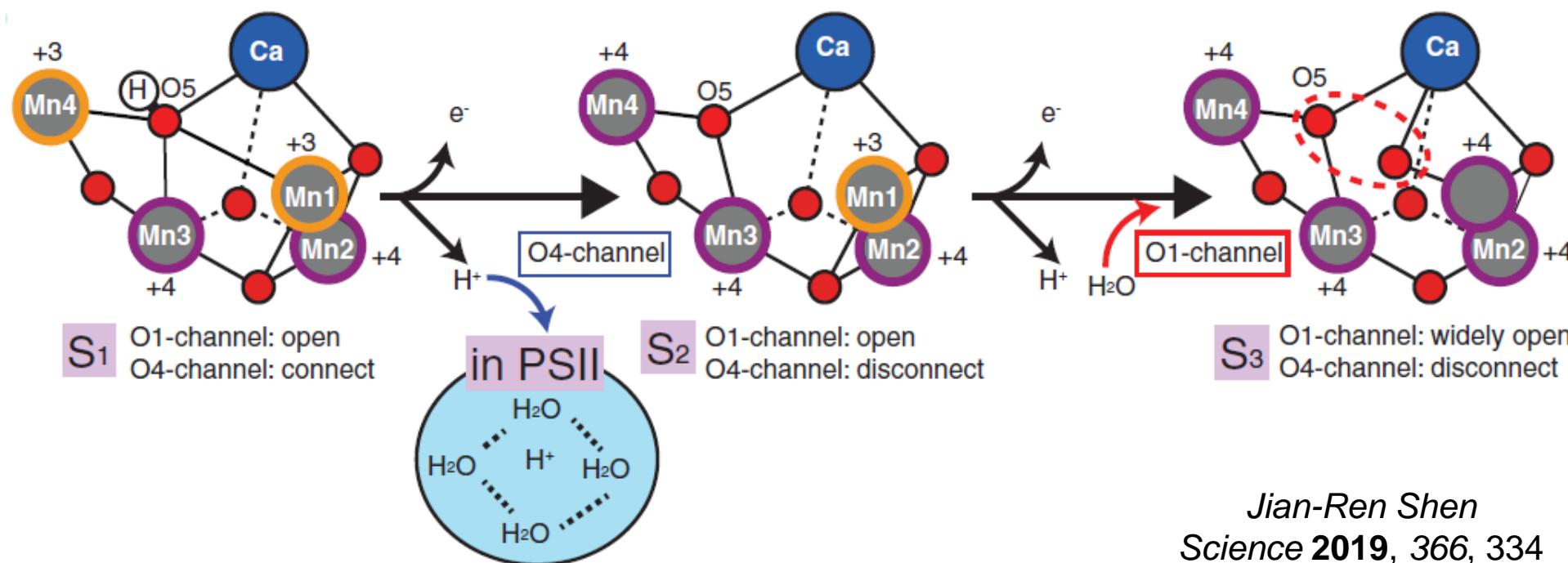
## Crystal Structure of Oxygen-evolving Center in Photosystem II (PSII) (Umean et al. Nature 2011, 473, 55)



# S1-S3 States observed by serial X-ray free-e laser

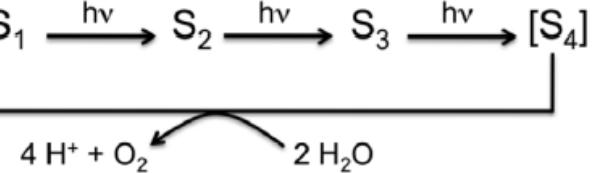
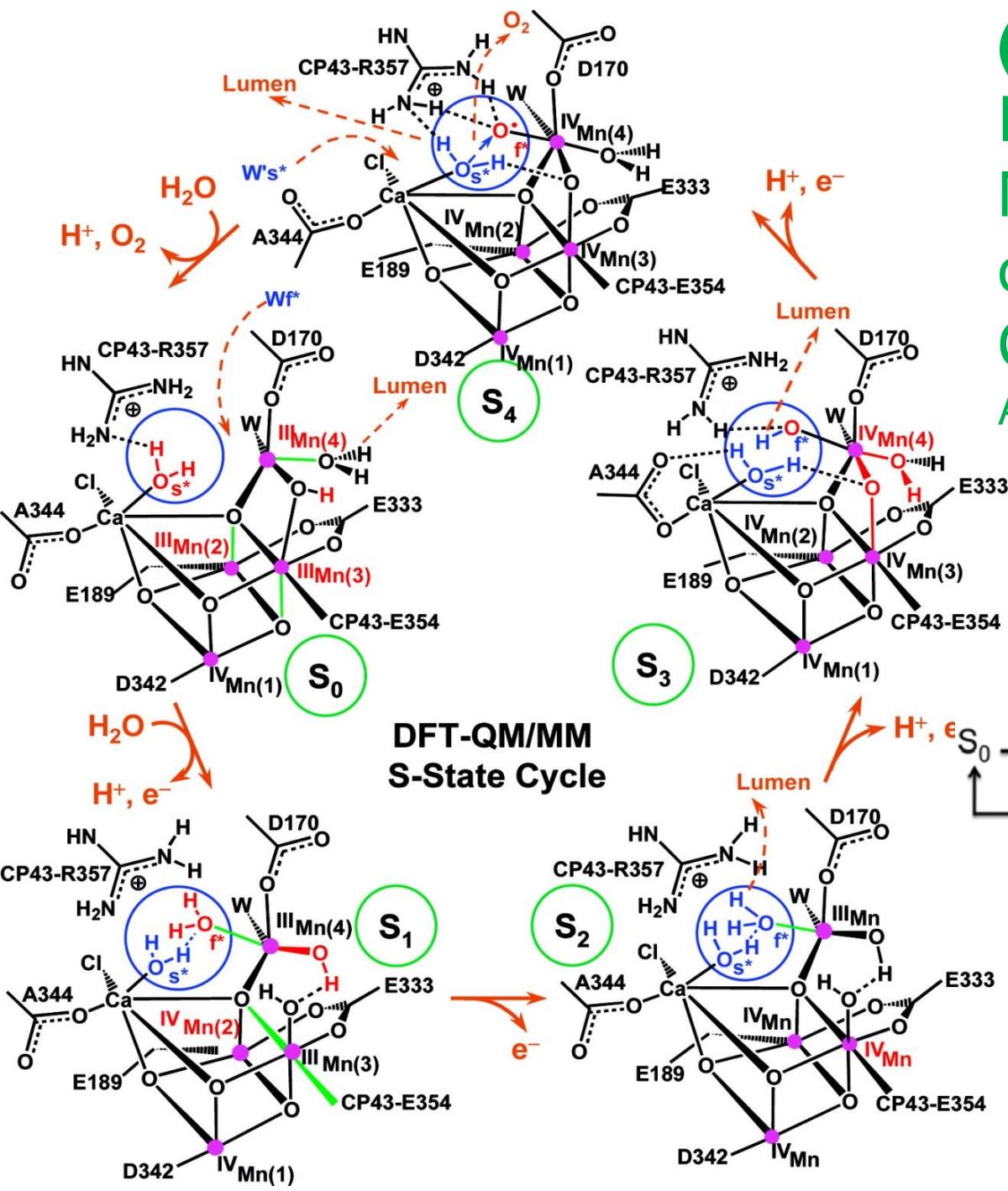


## Proposed Mechanism (Extra Info.)



# (Extra Info.)

## Proposed Mechanism based on A Computational Chemistry Method (J. Am. Chem. Soc. 2008, 3428)



Thermochemistry

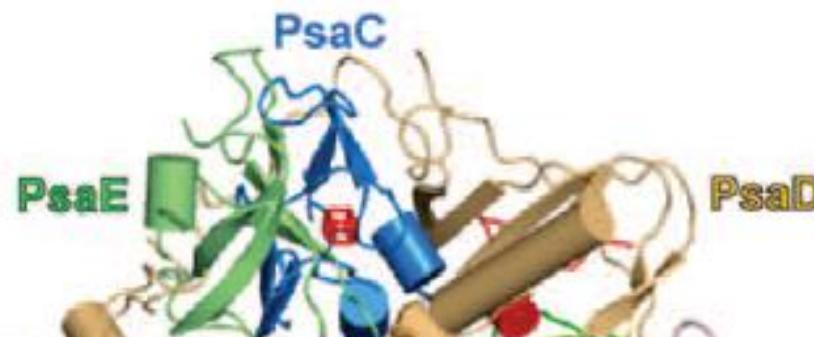
# Photosystem I (PSI)-Light-Harvesting Complex I (LHCI) supercomplex

(Qin et al. Science 2015, 348, 989) By 中国  
科学院植物研究所

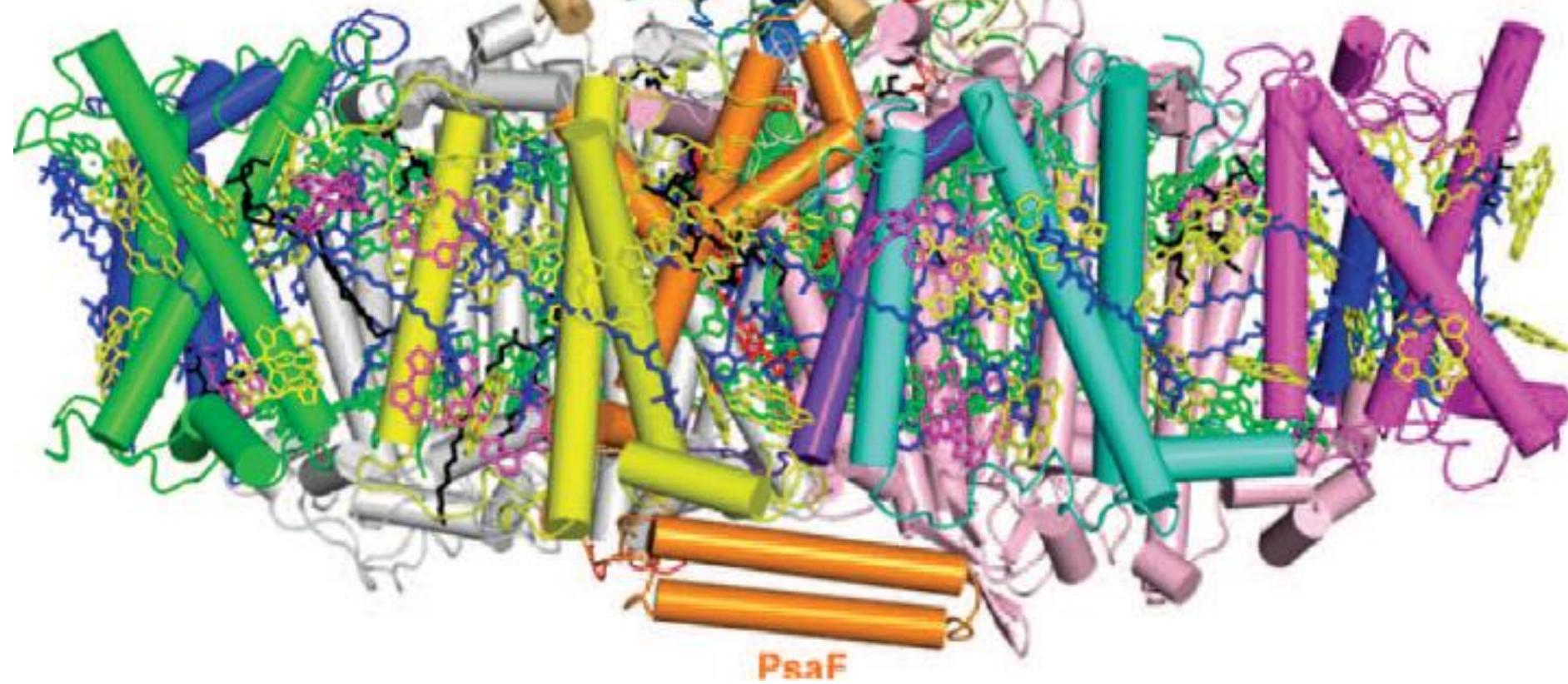
**(Extra Info.)**

**C**

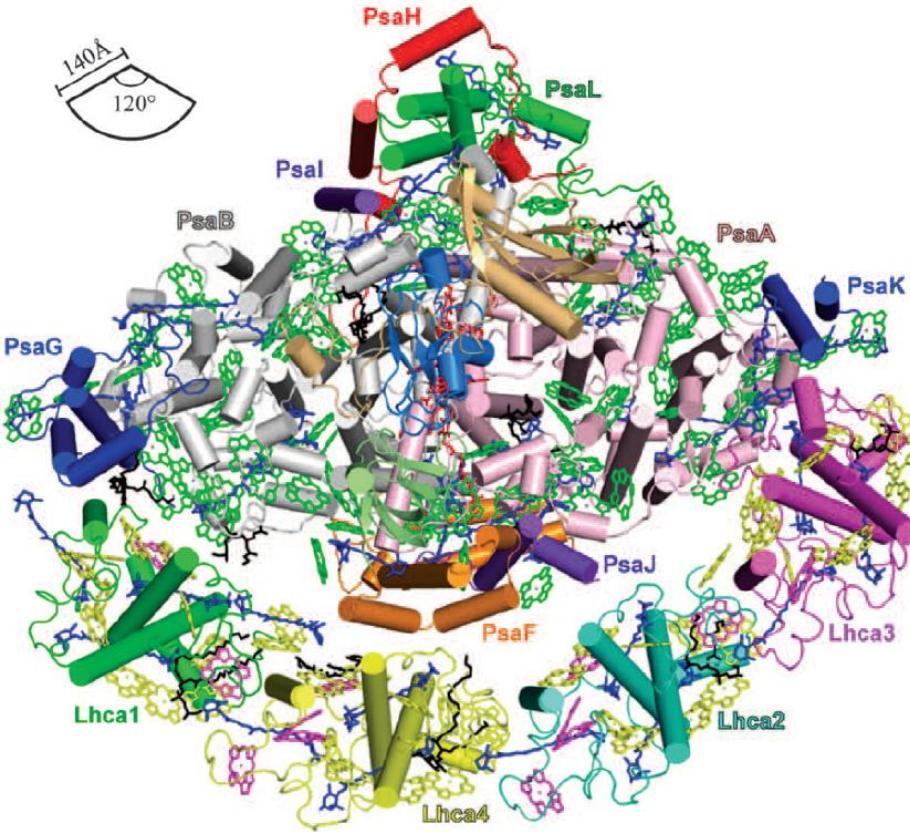
30Å  
40Å



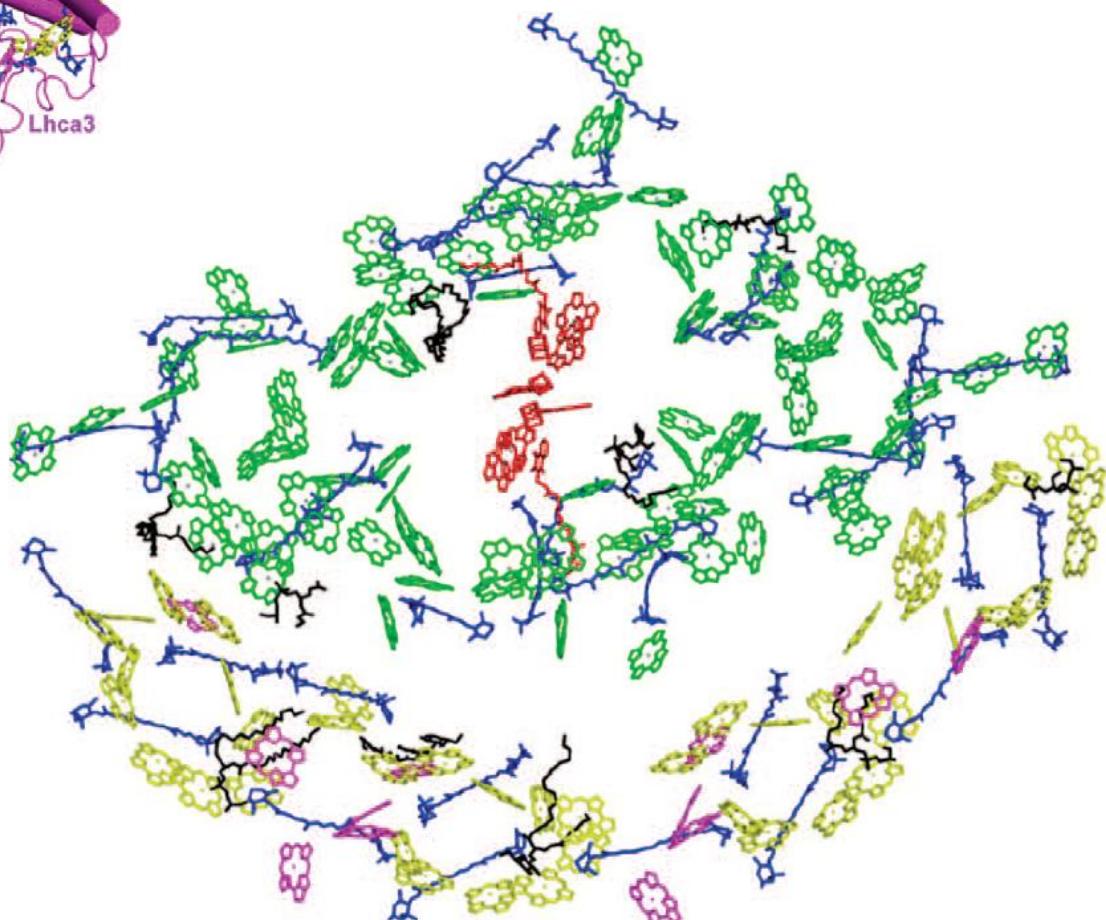
PsaF



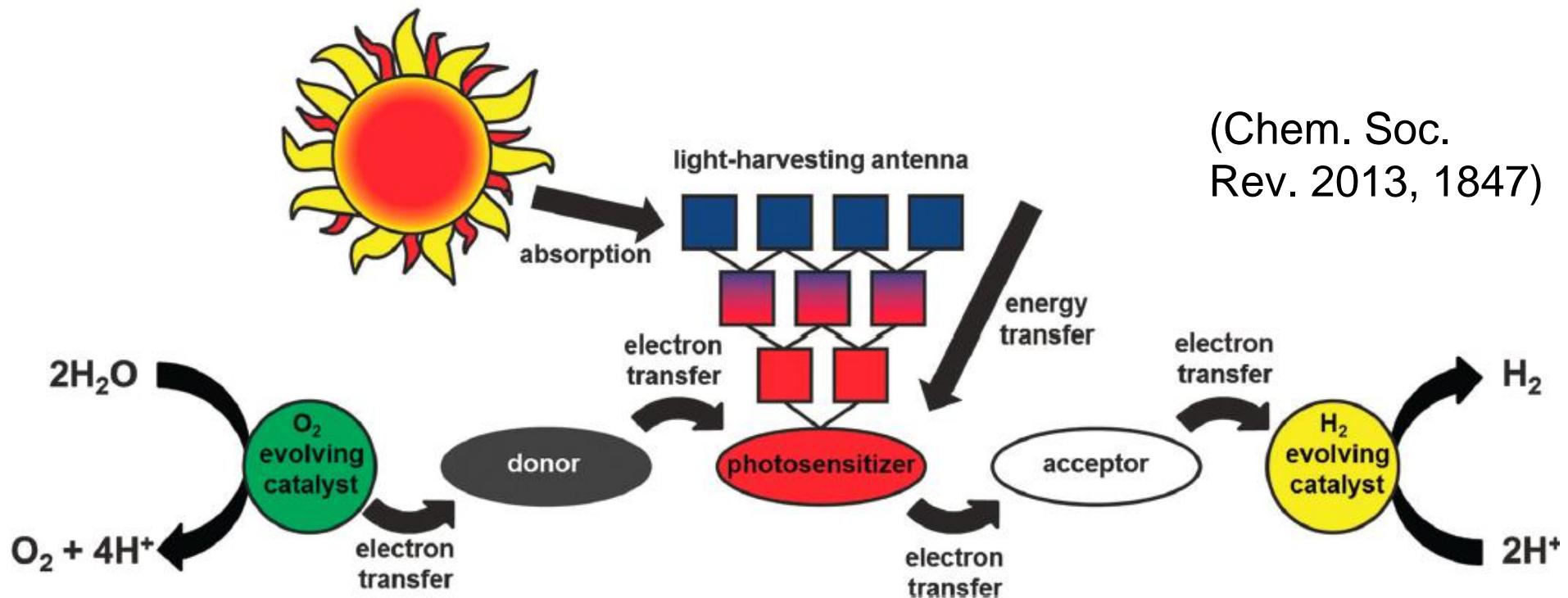
(Extra Info.)



## Arrangement of pigments & other cofactors



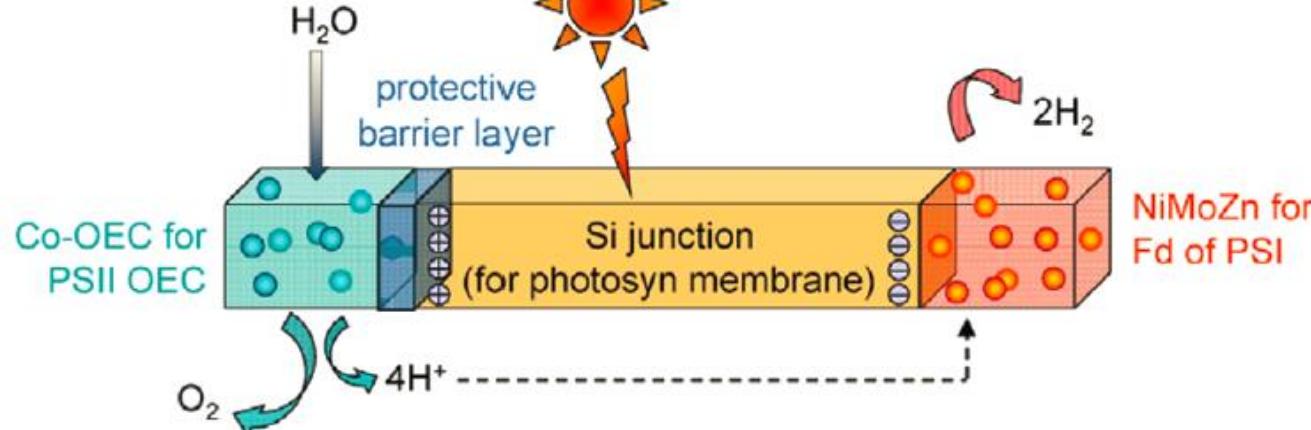
# (Extra Info.) Artificial Photosynthesis/Leaf: Water Splitting or H<sub>2</sub> Formation



(Chem. Soc.  
Rev. 2013, 1847)

(Acc. Chem.  
Res. 2012, 1847)

## (Extra Info.)



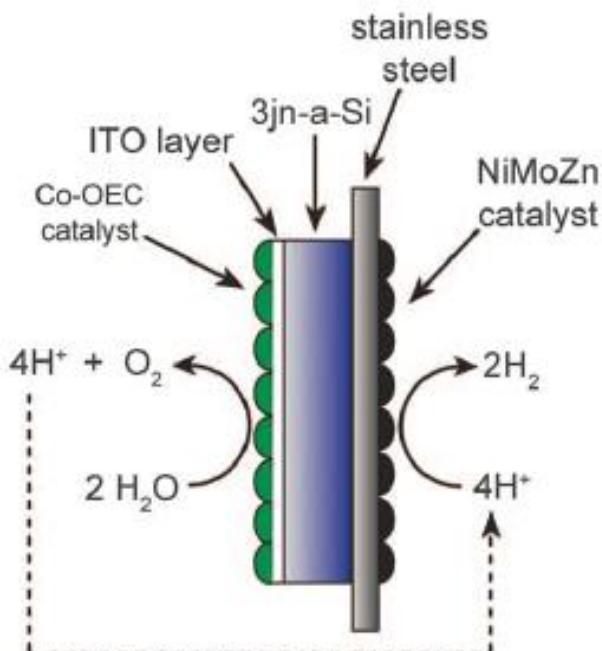
### Wireless Solar Water Splitting Using Silicon-Based Semiconductors and Earth-Abundant Catalysts

Steven Y. Reece *et al.*

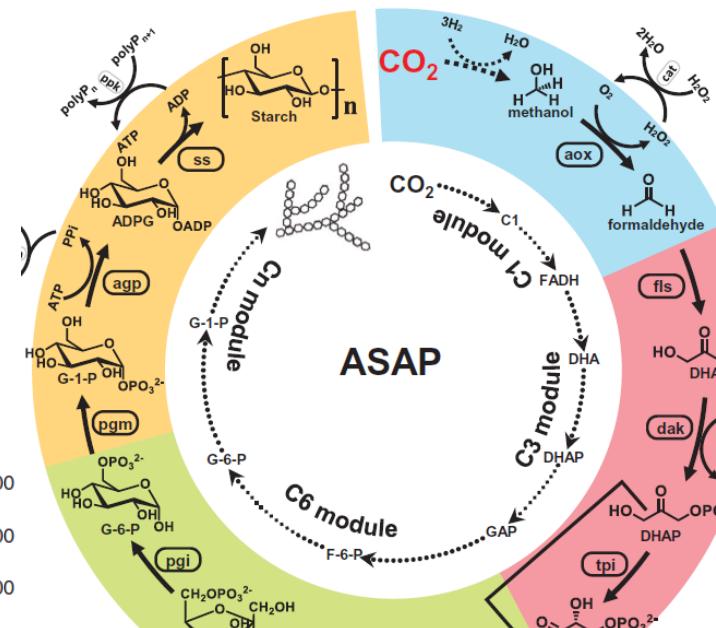
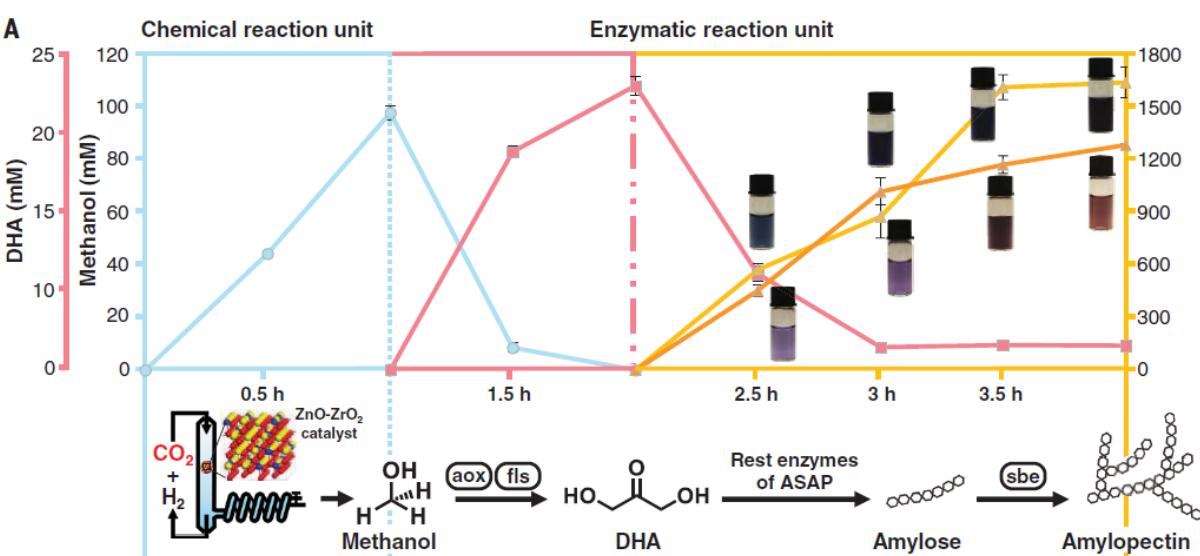
Science 334, 645 (2011);

DOI: 10.1126/science.1209816

#### wireless cell



# (Extra Info.) Cell-free chemoenzymatic starch synthesis from carbon dioxide



(Science  
2021, 1523)

Pathway	Substrate	Energy input	Target product	Titer (mg liter <sup>-1</sup> )	Time (hours)	Productivity (mg liter <sup>-1</sup> hour <sup>-1</sup> )	Starch synthesis rate* (nmol C min <sup>-1</sup> mg <sup>-1</sup> )
ASAP 1.0	Methanol	-	Amylose	30 ± 1	10	3.0 ± 0.1	0.15 ± 0.01
ASAP 2.0	Methanol	-	Amylose	230 ± 5	10	23 ± 1	2.0 ± 0.1
ASAP 3.0	CO <sub>2</sub>	H <sub>2</sub>	Amylose	1640 ± 86	4	410 ± 22	22 ± 1 <sup>†</sup>
ASAP 3.1	CO <sub>2</sub>	H <sub>2</sub>	Amylopectin	1280 ± 6	4	320 ± 2	17.2 ± 0.1 <sup>†</sup>
CETCH 5.4	NaHCO <sub>3</sub>	NADPH	Glyoxylate	40.0	1.5	26.7	3.87 <sup>‡</sup>
Calvin cycle	CO <sub>2</sub> and H <sub>2</sub> O	Solar	Starch	-	120 days	-	2.58 <sup>§</sup>



# Biofuels



Sugarcane 甘蔗

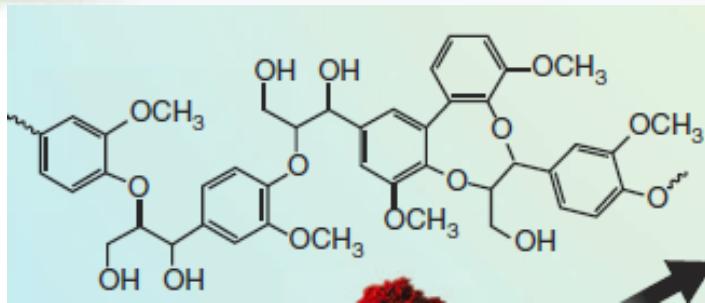
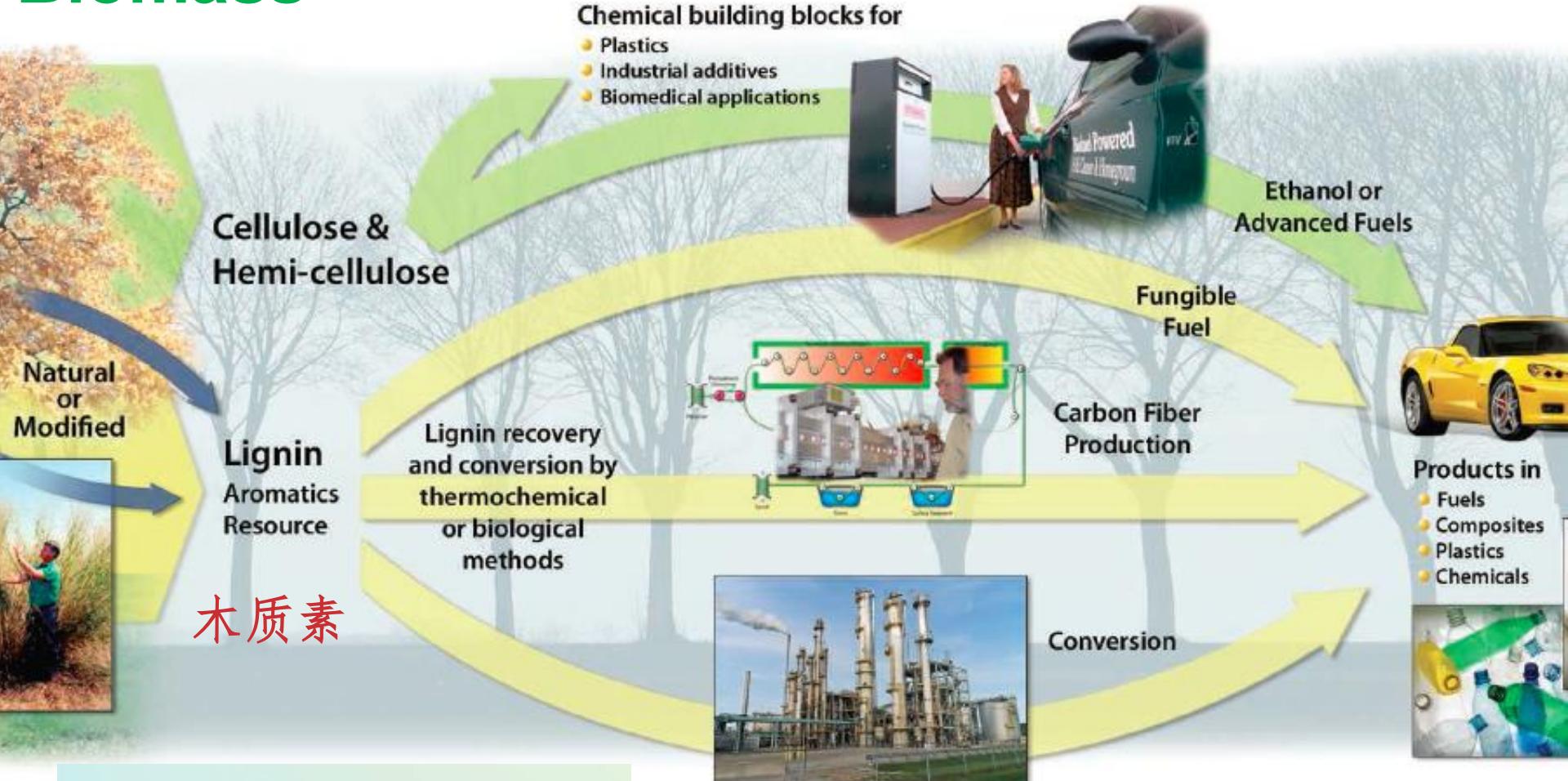


Ethanol fuel in Brazil  
food v.s. fuel

Thermochemistry



# (Extra Info.) Biofuels from Cellulosic (纤维质) Biomass



(Science 2014,  
344, 709)

Thermochemistry

# **Key Summary**

**Thermochemistry:** energy changes involving heat in chemical reactions

**Energy:** Work & Heat; Potential Energy & Kinetic Energy; System & Surroundings

**The 1<sup>st</sup> law of Thermochemistry:** Conversation of Energy; Internal energy; Endothermic & Exothermic; State function & Path function

**Enthalpy:** (Standard) Enthalpy of Reaction; Calorimetry; Heat Capacity; Hess's Law; Enthalpy of Formation



**Thank You for Your  
Attention!  
Any Questions?**