



INTERNATIONAL COLLEGE
OF PHARMACEUTICAL
INNOVATION

国际创新药学院

Fundamentals of Medicinal and Pharmaceutical Chemistry

FUNCHEM.28 Driving Forces Behind Chemical & Biological Reactions

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Factors Controlling Biological Phenomena

Factors affecting reaction rates

Rate law and orders of reactions

Molecularities of reactions

Pharmacokinetics

Catalysis and enzymes



Driving forces behind chemical & biological reactions

Importance of free energy in biochemical processes

Learning Objectives

- Driving forces behind chemical & biological reactions.
- Define the term 'thermodynamics'.
- Explain what you understand by an exothermic and endothermic process with the aid of energy profile diagrams.
- Explain the principles behind 'hot packs' used to treat muscular and arthritic pain and 'cold packs' used to treat sprains and swellings.
- Recall what you understand by 'standard conditions'.
- Define 'standard enthalpy of formation', 'standard enthalpy of combustion' and 'standard enthalpy of reaction'.
- State units of enthalpy.
- Recall the first law of thermodynamics.
- Recall standard rules for manipulating thermochemical equations.
- Recall and apply Hess's Law to work out the standard enthalpy change for a specified reaction.

Consider a chemical equation . . .

- Does not help you predict whether the reaction is likely to occur
- Thermodynamics: **Tool used to predict whether a reaction is spontaneous or not**
- Spontaneous reactions: **occur of their own accord**

e.g. Waterfall

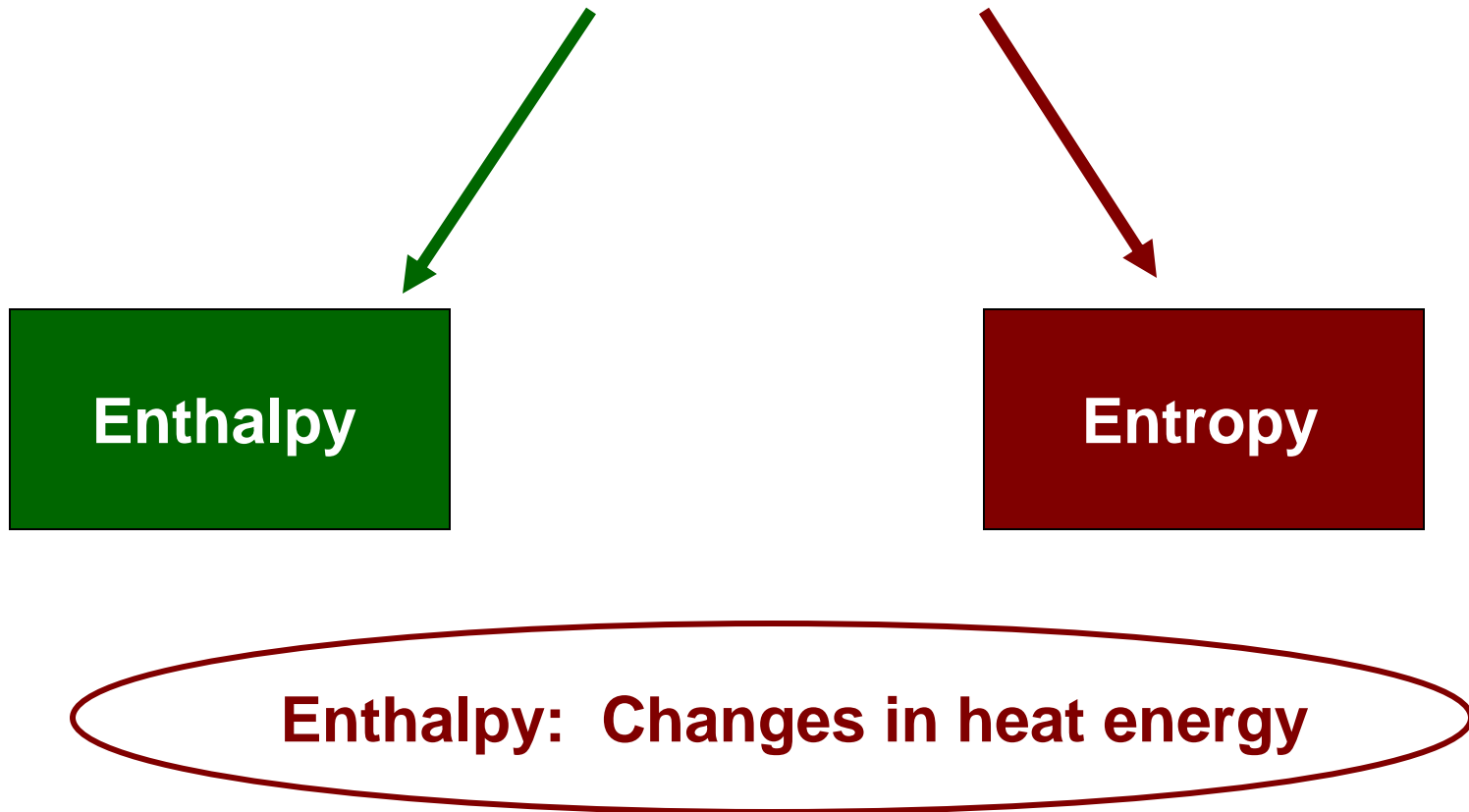


e.g. Cars rust



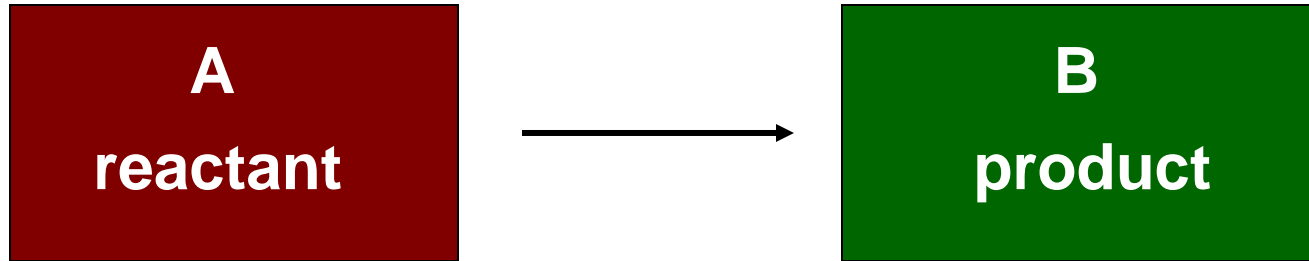
Thermodynamics

The driving force behind chemical and biological reactions.



Thermodynamics

Most reactions (chemical or biological)
occur with changes in energy



- Cannot measure the energy of A directly (E_1)
- Cannot measure the energy of B directly (E_2)
- **Can measure the energy change which occurs during the reaction**

$$\Delta E = E_2 - E_1$$

DELTA (Δ)
= CHANGE

product **reactants**

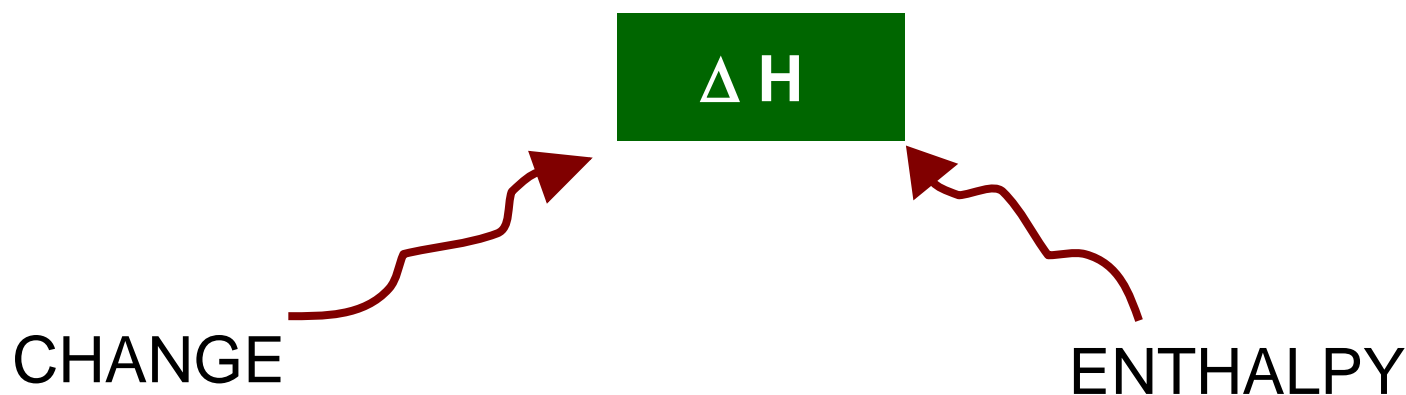
Thermodynamics

Because the energy involved is heat:

Instead of energy = E

We use

Enthalpy = H



Units = kJ mol⁻¹

kJ of energy per mole of reactant

Thermodynamics

EXOTHERMIC REACTION

out

heat



energy
H

Reactants

give out
heat energy

Products

start

CH₄

2O₂

CO₂

2H₂O

finish

Surroundings at
room temperature

Surroundings
gain heat

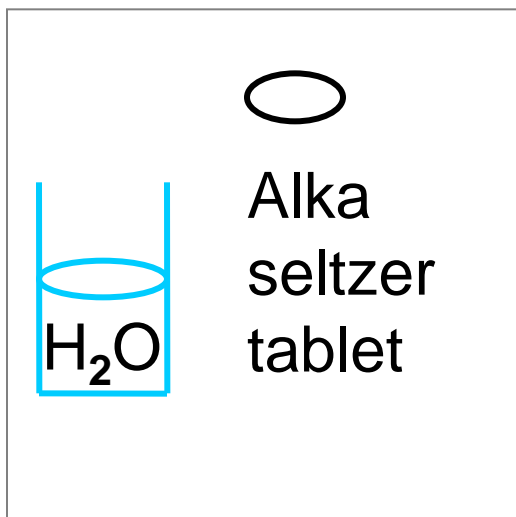
Thermodynamics

ENDOTHERMIC REACTION: Heat taken in

in

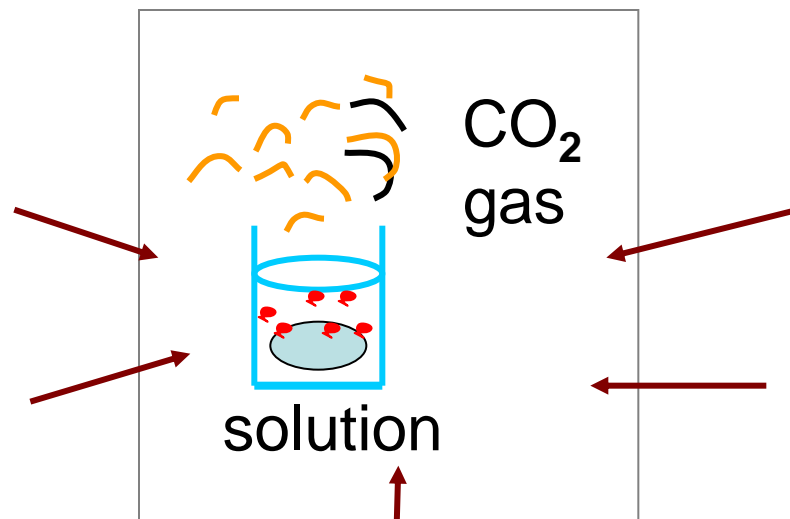
heat

start



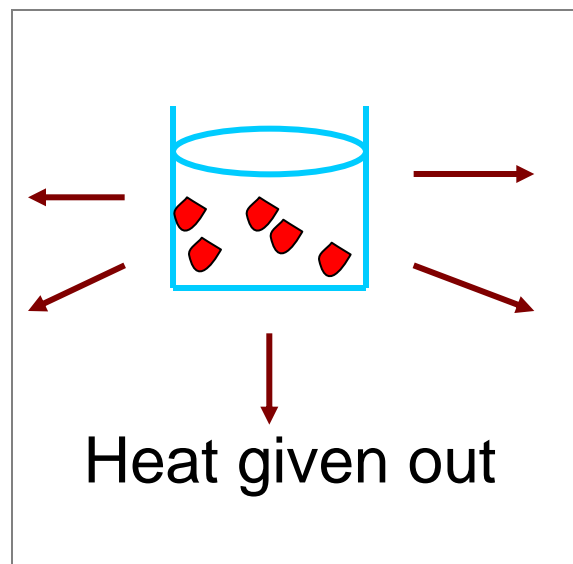
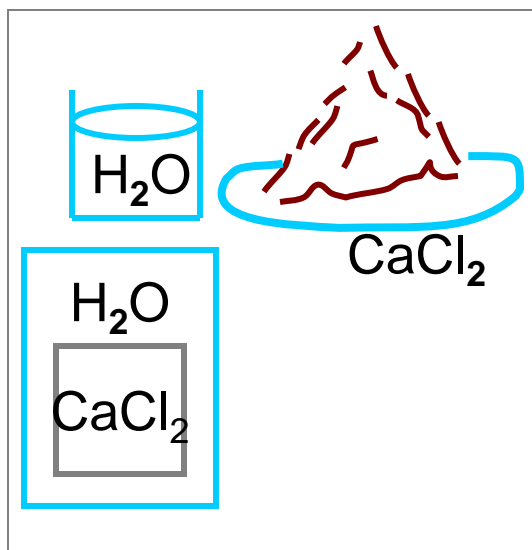
Surroundings at
room temperature

finish

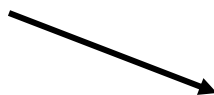


Surroundings lose
heat

Hot Pack – used to treat muscle and arthritic pain



40g CaCl_2 in 100 ml H_2O



EXOTHERMIC REACTION

20°C
room temperature

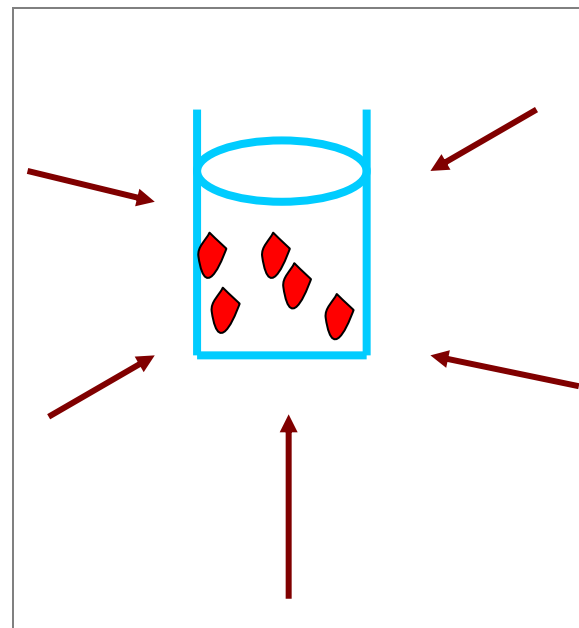
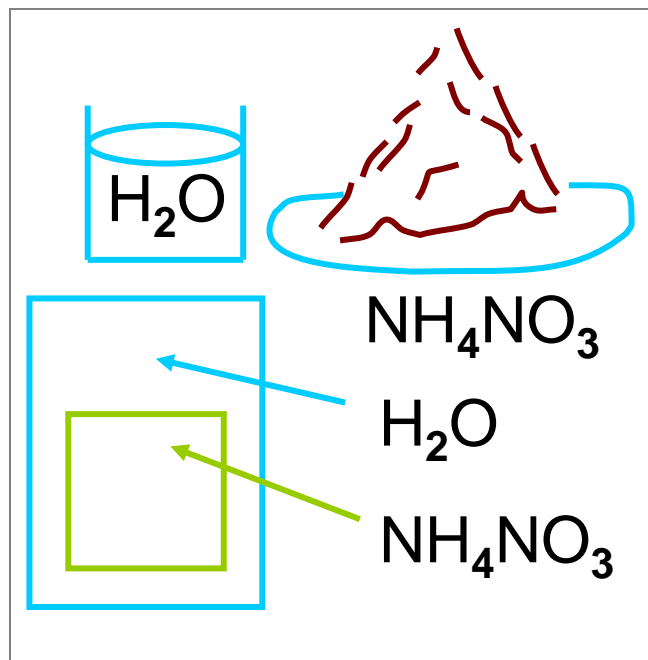


90 °C

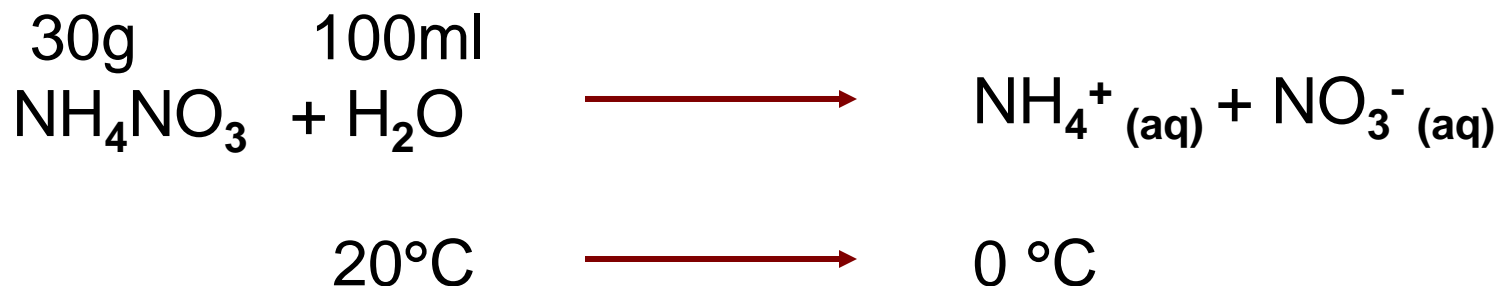
surroundings

Cold Pack – used to treat sprains & swellings

Heat taken in
from surroundings



ENDOTHERMIC



Standard Enthalpy Change

Calorimetry - technique used to measure the heat energy which accompanies a reaction

STANDARD ENTHALPY CHANGE:

Enthalpy change which occurs at temp **298K** and **1 atm** pressure

change

ΔH°

enthalpy

*Standard
Temp = 298 K
Pressure = 1 atm*

Standard Enthalpy Change

Standard Enthalpy Change of *Formation* ΔH°_f

Standard Enthalpy Change of *Combustion* ΔH°_c

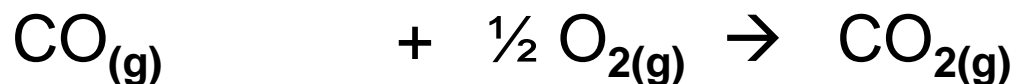
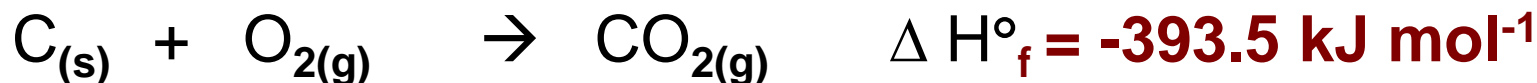
Standard Enthalpy of *Reaction* $\Delta H^\circ_{\text{rxn}}$

Standard Enthalpy Change of *Formation*

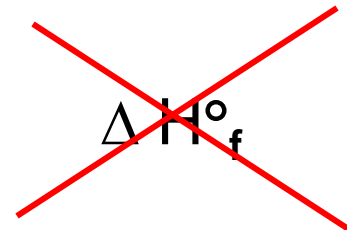
$$\Delta H^\circ_f$$

$$\Delta H^\circ_f$$

Enthalpy change that occurs when **1 mole**
of compound is formed from its
uncombined elements at
STANDARD temp. = 298 K ; pressure 1 atm



Not uncombined
element



Standard Enthalpy Change of Combustion

ΔH°_c

$$\Delta H^\circ_c$$

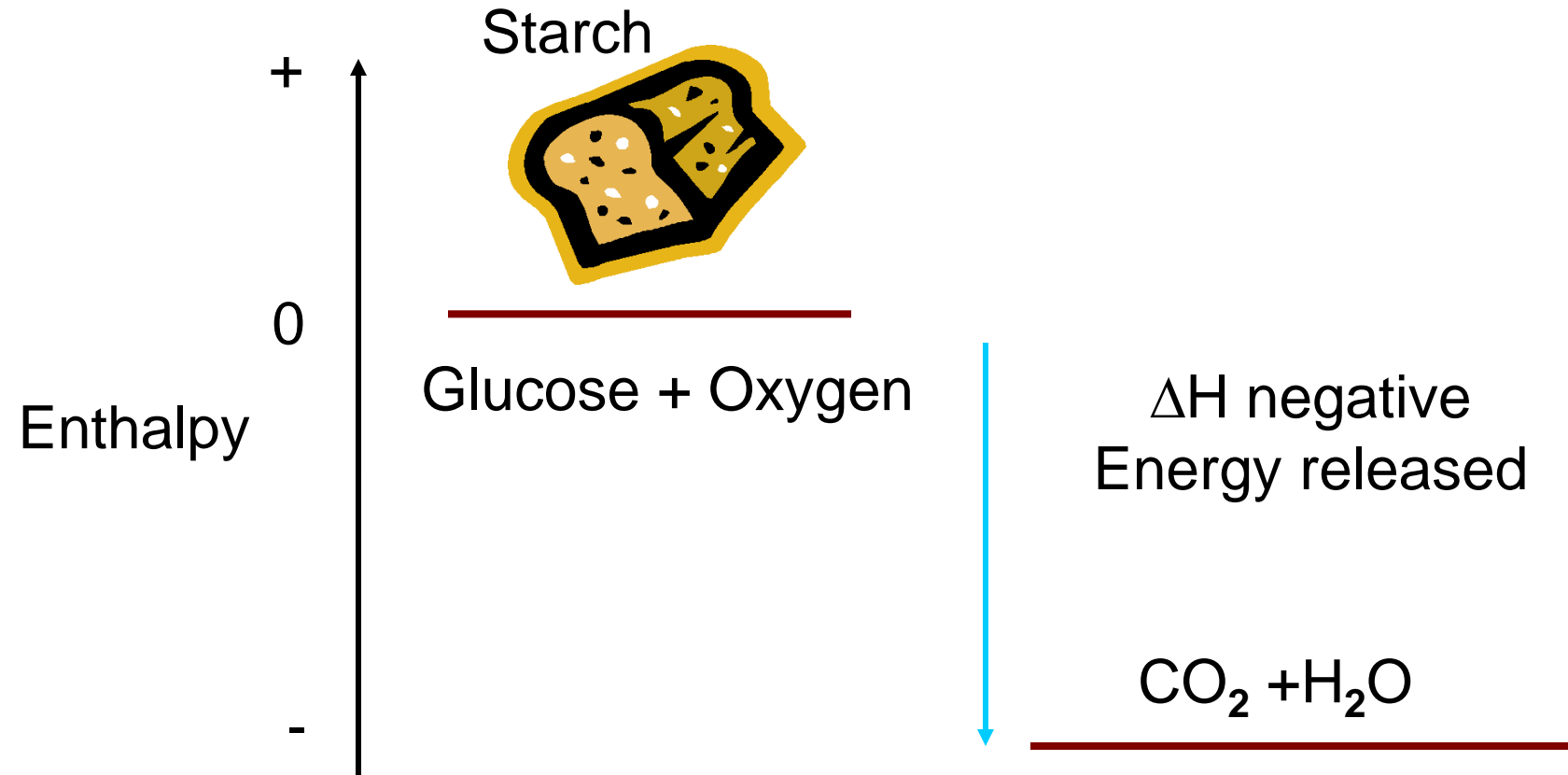
Enthalpy change that occurs when **1 mole** of an element or compound **is burned in excess** O_2 at 298k + 1 atm.

Example:



$$\Delta H^\circ_c = -2801 \text{ kJ mol}^{-1}$$

Metabolism



Combustion is always **highly exothermic**.
Think of fires, gas cookers etc. - ΔH

Standard Enthalpy of *Reaction*

$$\Delta H^{\circ}_{\text{rxn}}$$

More general term:

$$\Delta H^{\circ}_{\text{rxn}}$$

reaction



$\Delta H^{\circ}_{\text{c}}$: standard enthalpy of **combustion** of C

$\Delta H^{\circ}_{\text{f}}$: standard enthalpy of **formation** of CO_2

$\Delta H^{\circ}_{\text{rxn}}$: standard enthalpy of **reaction** of $\text{C} + \text{O}_2$

Standard Enthalpy of *Reaction*



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

How do you measure ΔH directly?

FIRST LAW OF THERMODYNAMICS

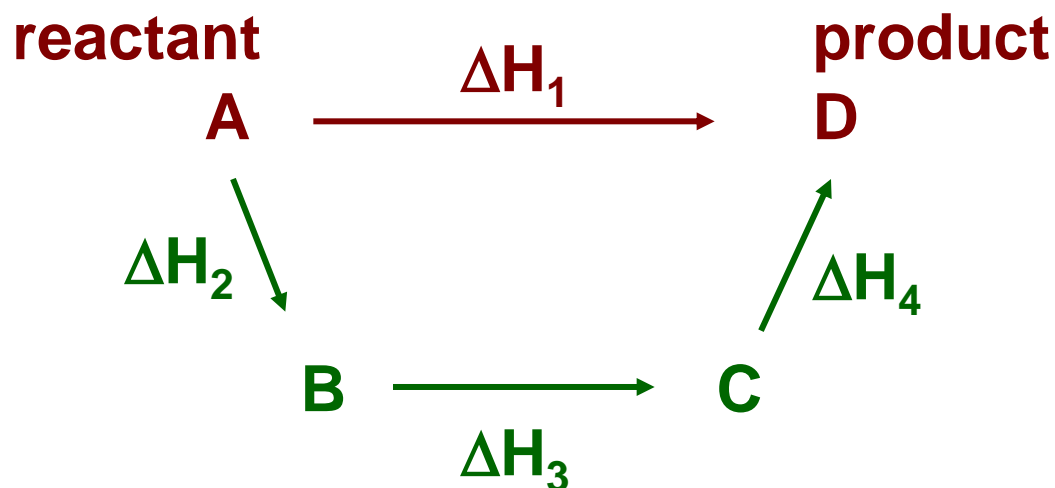
Energy cannot be created nor destroyed,
it can only be converted from one form
to another

Standard Enthalpy of *Reaction*

HESS'S LAW:

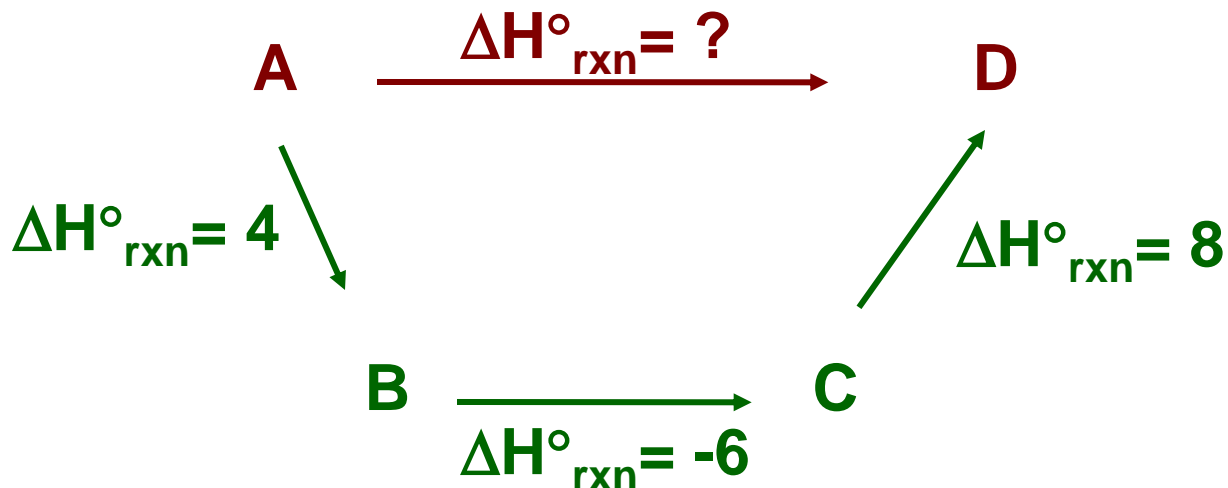
The enthalpy change of a reaction is the same regardless of the pathway by which the reaction occurs.

Hess's Cycle



$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

Standard Enthalpy of *Reaction*



Rules for thermochemical reactions

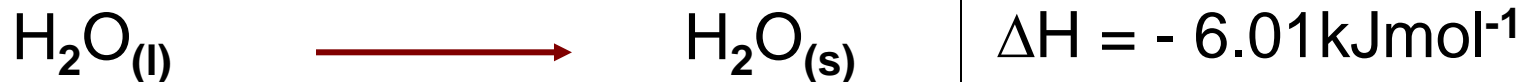
1. Must have balanced equations
2. Must specify states of the reactants and products i.e. solids/liquids/gases/aqueous



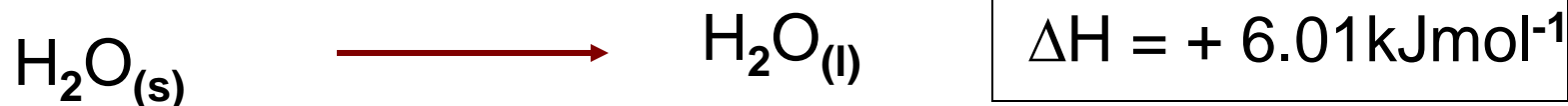
Rules for thermochemical reactions

3. Reverse Reaction : Reverse Sign

Ice forming



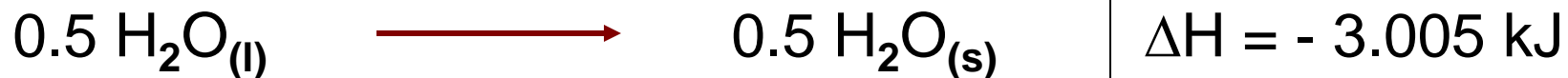
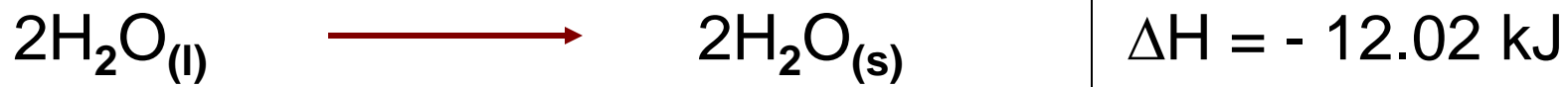
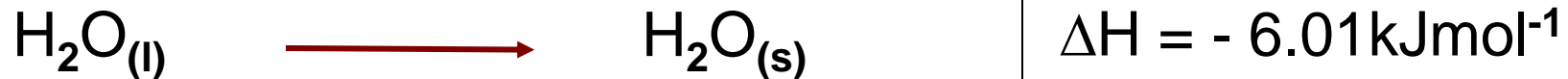
Ice melting



Rules for thermochemical reactions

4. ΔH depends on the amount reacting

Ice forming



Rules for thermochemical reactions

5. Enthalpy of formation of an element in its most stable form

$$= 0$$

$$\Delta H^\circ_f \text{ O}_2 = 0$$

$$\Delta H^\circ_f \text{ H}_2 = 0$$

$$\Delta H^\circ_f \text{ Na} = 0$$

Determine ΔH_{rxn} - Draw a Hess Cycle

1. Write out the equation you require and balance it.



2. Write equations to represent information given
3. Aim to find a sequence of reactions, the sum of which is the reaction of interest
4. Solve

Example 1

Determine the molar heat of combustion of methanol.



Given:

$$\Delta H^\circ_f \quad (\text{CO}_2)_{(g)} \quad = \quad - 393.5 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_f \quad (\text{H}_2\text{O})_{(g)} \quad = \quad - 241.8 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_f \quad (\text{CH}_3\text{OH})_{(g)} \quad = \quad -239.0 \text{ kJ mol}^{-1}$$

Molar heat of combustion of methanol

$$\Delta H^\circ_c \quad (\text{CH}_3\text{OH})$$



Example 1

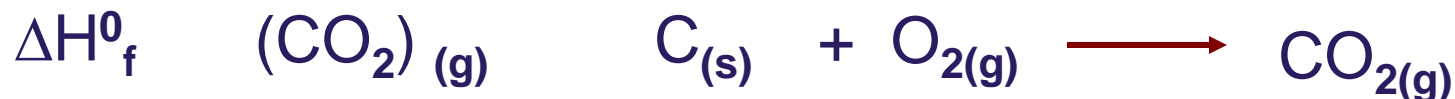
Step 1: Write out equation you require and balance it



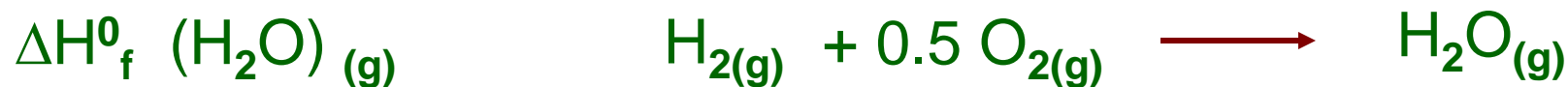
BALANCED

Example 1

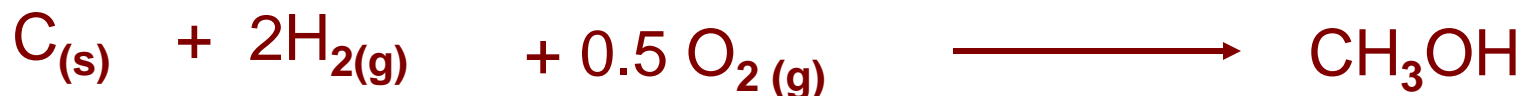
Step 2: Write out equations for information given



$$\Delta H^{\circ}_f = - 393.5 \text{ kJ mol}^{-1}$$



$$\Delta H^{\circ}_f = - 241.8 \text{ kJ mol}^{-1}$$



$$\Delta H^{\circ}_f = - 239 \text{ kJ mol}^{-1}$$

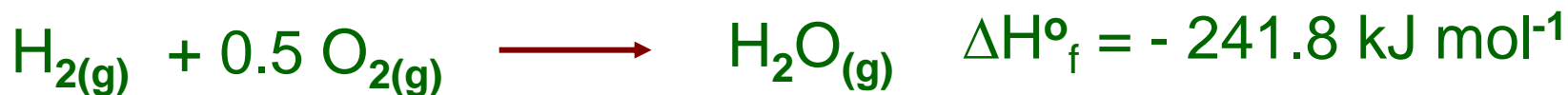
Example 1

Step 3: Aim to find a sequence of reactions, the sum of which is the reaction of interest:

Equation required:



Given:



Recall: $\Delta H^\circ_{\text{f}}(\text{O}_2)$

Enthalpy of formation of element in natural form = 0

Example 1

Step 3: Rearrange reactions to give the reaction of interest:

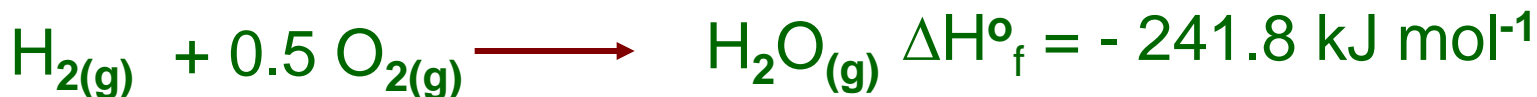
Equation required:



Given:



OK!



X 2



REVERSE

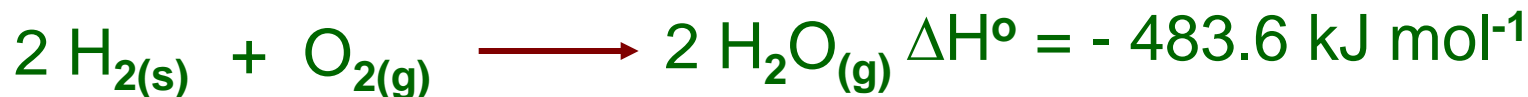
Example 1

Step 3: Rearrange reactions to give the reaction of interest:

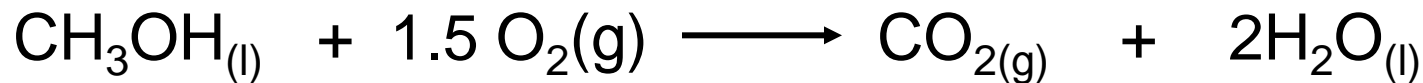
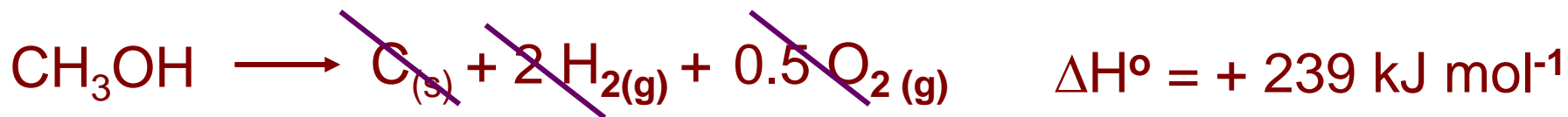
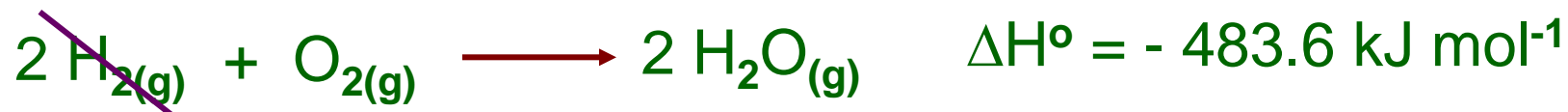
Equation required:



Rearranged:



Does it balance?



$$\Delta H^\circ_c = -393.5 - 483.6 + 239 = -638.1 \text{ kJ mol}^{-1}$$

Example

Try this one: Calculate ΔH^0_{rxn} for



Given:

ΔH^0_f

$$\text{CO}_2 = -393.5 \text{ kJ mol}^{-1}$$

$$\text{H}_2\text{O} = -285.8 \text{ kJ mol}^{-1}$$

$$\text{C}_6\text{H}_{6(l)} = +49.0 \text{ kJ mol}^{-1}$$

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- Define the term 'thermodynamics'.
- Explain what you understand by an exothermic and endothermic process with the aid of energy profile diagrams.
- Explain the principles behind 'hot packs' used to treat muscular and arthritic pain and 'cold packs' used to treat sprains and swellings.
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