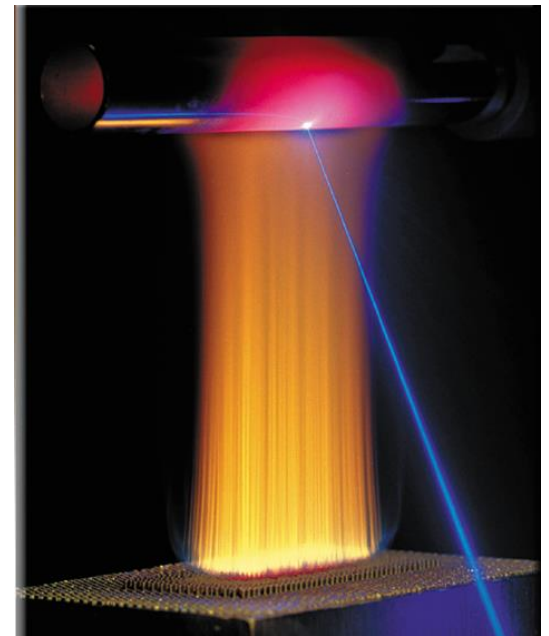
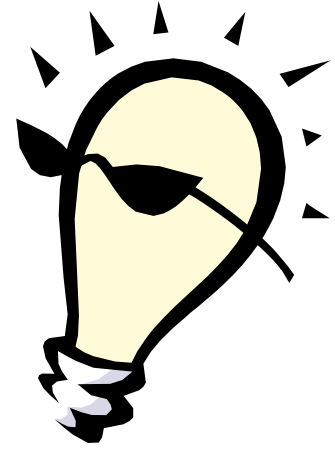


Thermochemistry



Energy is the capacity to do work

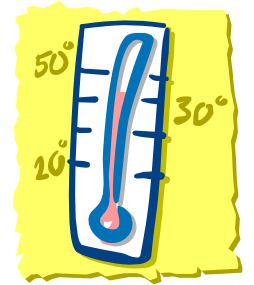
- **Thermal energy** is the energy associated with the random motion of atoms and molecules
- **Chemical energy** is the energy stored within the bonds of chemical substances
- **Nuclear energy** is the energy stored within the collection of neutrons and protons in the atom
- **Electrical energy** is the energy associated with the flow of electrons
- **Potential energy** is the energy available by virtue of an object's position



Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.

Temperature is a measure of the **thermal energy**.



Temperature \neq Thermal Energy



90°C

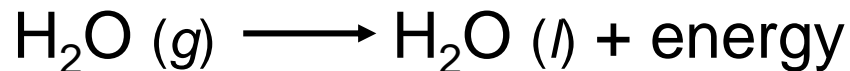
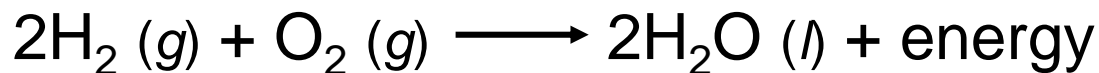


40°C

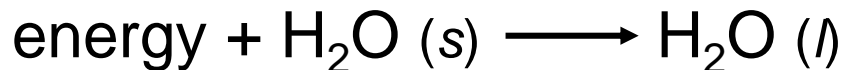
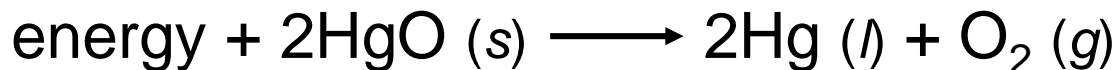
greater thermal energy

- The study of the energy transferred as heat during the course of chemical reactions is called **thermochemistry**
- Thermochemistry is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and the surroundings.
- Thus we can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q with a change in internal energy (if the reaction occurs at constant volume) or a change in enthalpy (if the reaction occurs at constant pressure).
- Conversely, if we know ΔU or ΔH for a reaction, we can predict the energy (transferred as heat) the reaction can produce.

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.

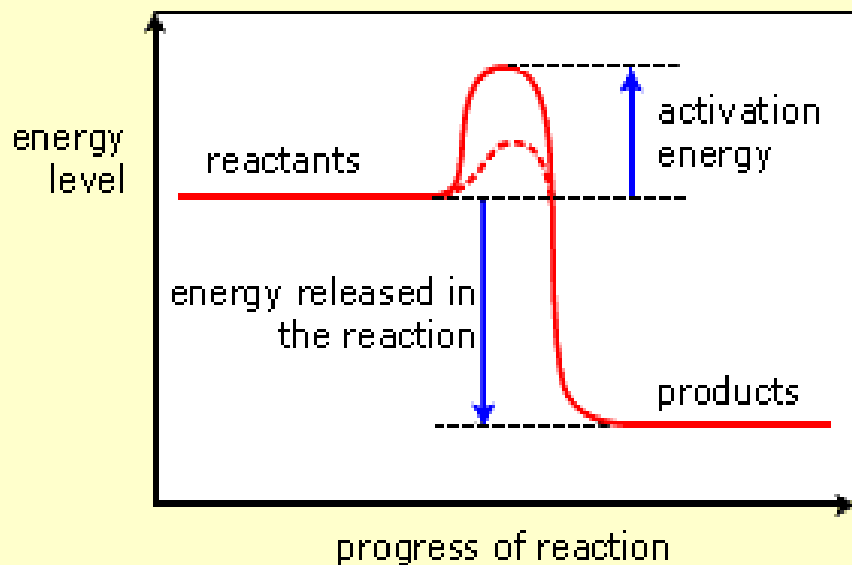


Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

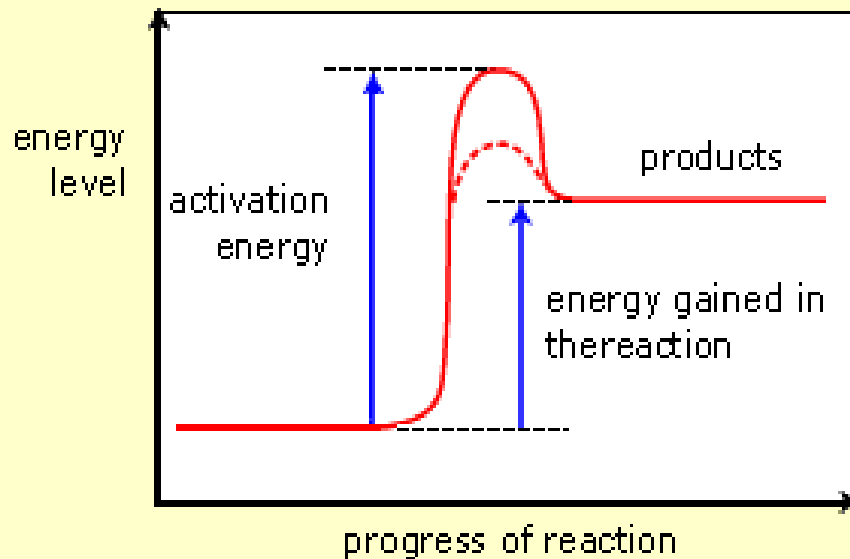


Exothermic & Endothermic reactions

Energy levels in an exothermic reaction



Energy levels in an endothermic reaction



Exothermic reaction

- Energy is released.
- Reaction vessel becomes hotter.
- Temperature inside reaction vessel increases.

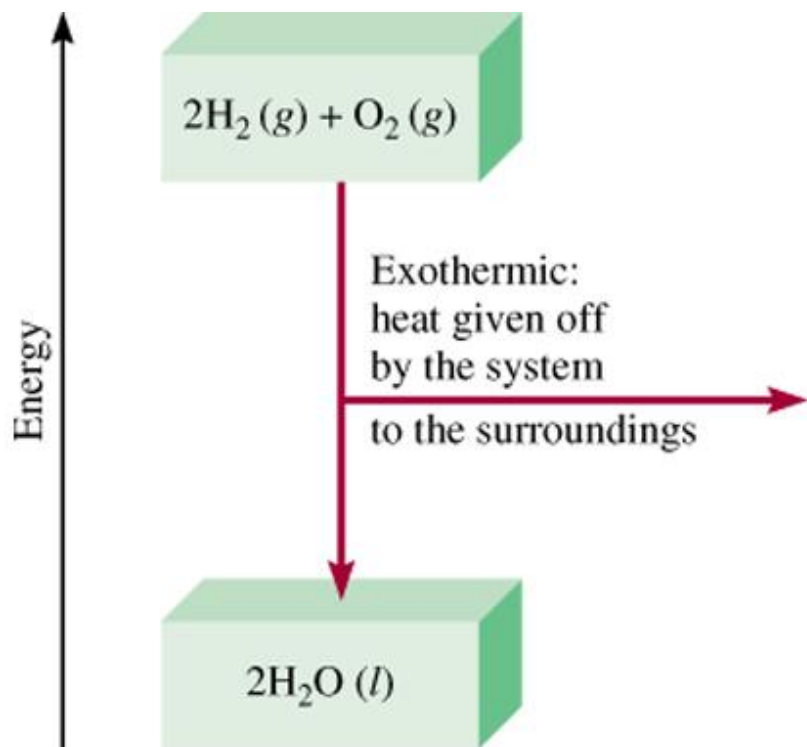
Endothermic reaction

- Energy is absorbed.
- Reaction vessel becomes cooler.
- Temperature inside reaction vessel decreases.

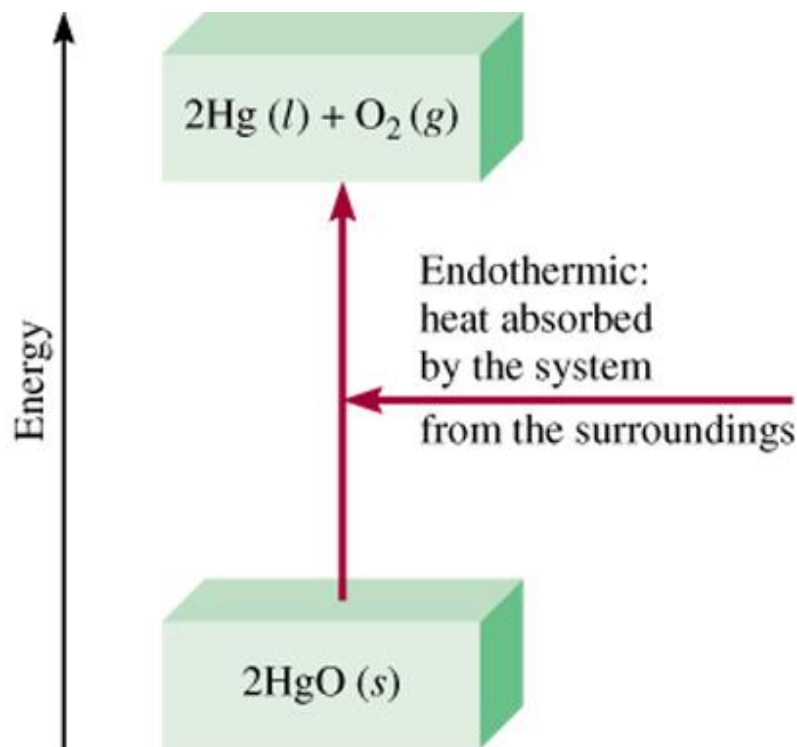
Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

ΔH = heat given off or absorbed during a reaction **at constant pressure**

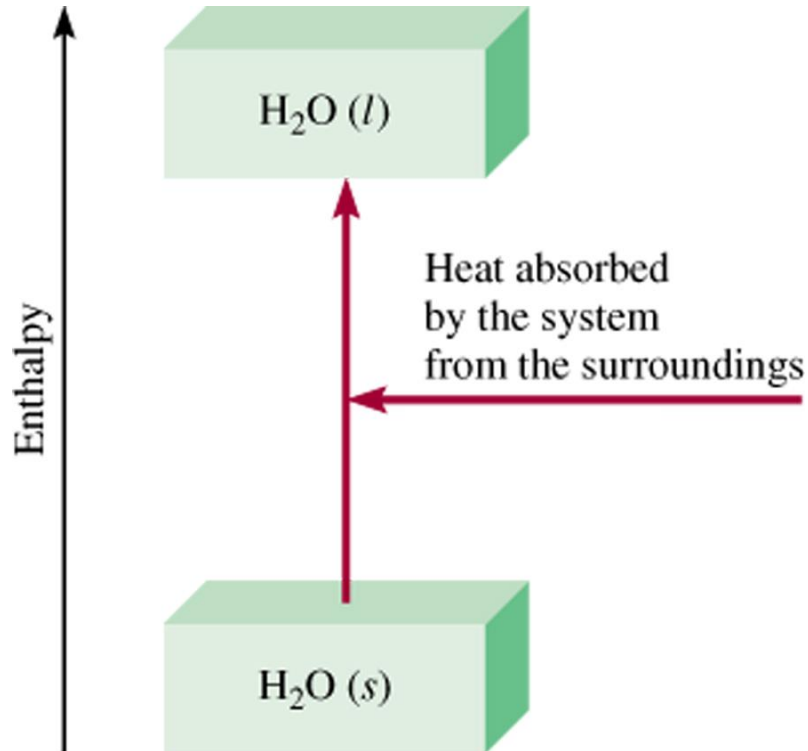


$$H_{\text{products}} < H_{\text{reactants}}$$
$$\Delta H < 0 \text{ (-ve)}$$



$$H_{\text{products}} > H_{\text{reactants}}$$
$$\Delta H > 0 \text{ (+ve)}$$

Thermochemical Equations



Is ΔH negative or positive?

System absorbs heat

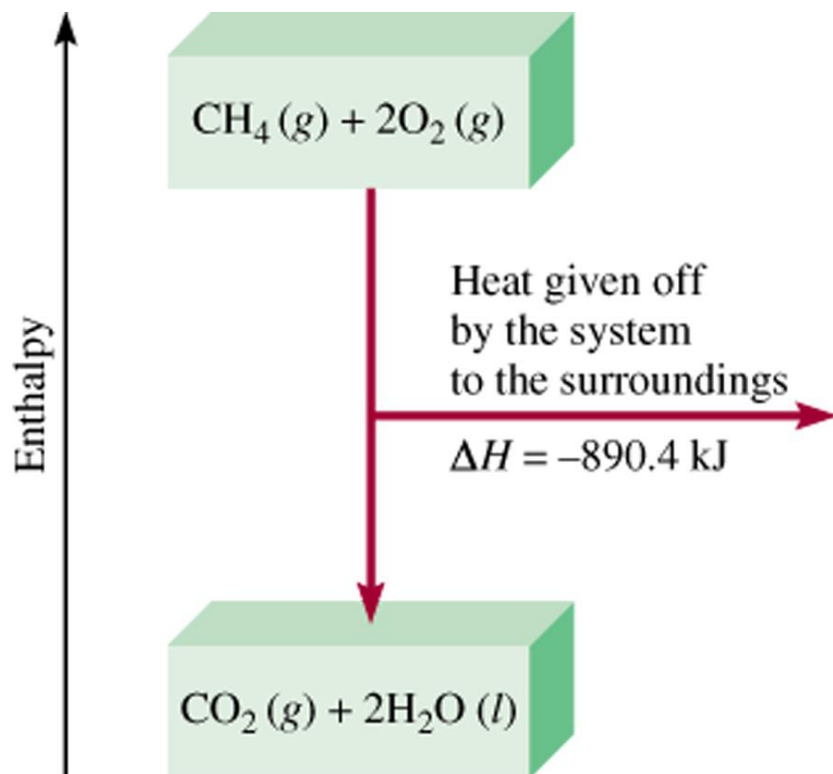
Endothermic

$\Delta H = +ve$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0°C and 1 atm.



Thermochemical Equations



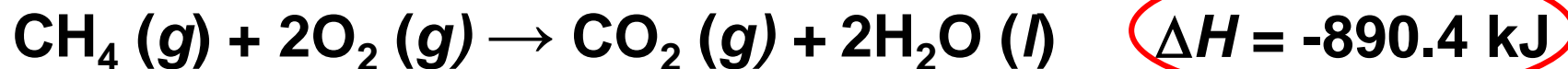
Is ΔH negative or positive?

System gives off heat

Exothermic

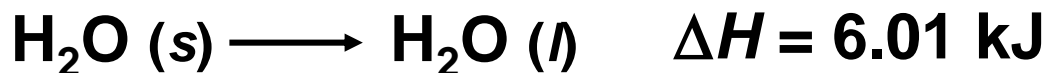
$\Delta H = -ve$

890.4 kJ are released for every 1 mole of methane that is combusted at 25°C and 1 atm.



Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance



- If you reverse a reaction, the sign of ΔH changes

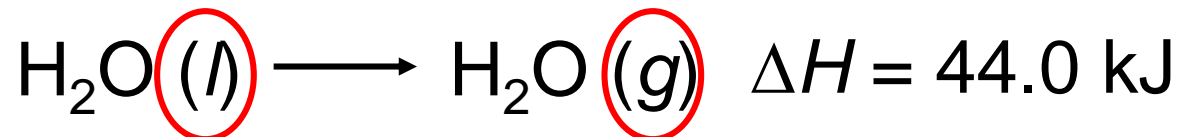
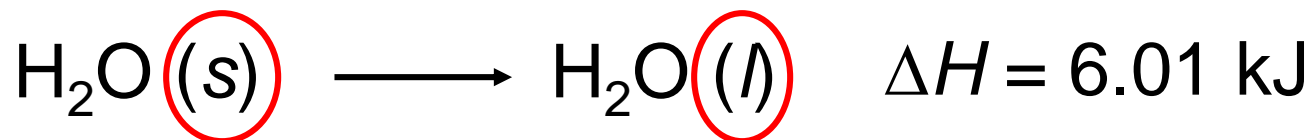


- If you multiply both sides of the equation by a factor n , then ΔH must change by the same factor n .



Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.



How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?



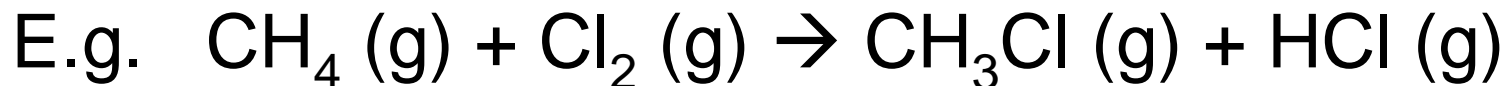
$$266 \text{ g } \cancel{\text{P}_4} \times \frac{1 \cancel{\text{ mol P}_4}}{123.9 \cancel{\text{ g P}_4}} \times \frac{3013 \text{ kJ}}{1 \cancel{\text{ mol P}_4}} = 6470 \text{ kJ}$$

Heat of Reaction (Enthalpy of Reaction)

- **Enthalpy change in a reaction**, which may be obtained from $\Delta_f H^\circ$ of products and reactants
Reactants \rightarrow Products

$$\Delta H_r^\circ = \sum_{\text{products}} n_p \Delta H_{f, \text{prod}}^\circ - \sum_{\text{reactants}} n_R \Delta H_{f, \text{reaction}}^\circ$$

v_i , stoichiometric coefficient, + ve products,
- ve reactants



- The **specific heat capacity** (C_p) of a substance is the amount of heat (q) required to raise the temperature of **one gram** of the substance by **one degree Celsius**.
- The **heat capacity** (C) of a substance is the amount of heat (q) required to raise the temperature of a **given quantity** (m) of the substance by **one degree Celsius**.

$$C = m C_p$$

Table 6.1 The Specific Heats of Some Common Substances

Substance	Specific heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502

Heat (q) absorbed or released:

$$q_p = m C_p \Delta t$$

$$q_p = C \Delta t$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

How much heat is given off when an 869 g iron bar cools from 94°C to 5°C?

$$C_p \text{ of Fe} = 0.444 \text{ J/g} \cdot ^\circ\text{C}$$

$$\Delta t = t_{\text{final}} - t_{\text{initial}} = 5^\circ\text{C} - 94^\circ\text{C} = -89^\circ\text{C}$$

$$q_p = m C_p \Delta t = 869 \text{ g} \times 0.444 \text{ J/g} \cdot ^\circ\text{C} \times -89^\circ\text{C}$$
$$= -34,000 \text{ J}$$

Calculating the heat absorbed by the solution

Heat = mass of solution × specific heat capacity × change in temp.
(J) (g) ($\text{J K}^{-1} \text{g}^{-1}$) (K or $^{\circ}\text{C}$)

$$q_p = m \times C_p \times \Delta T$$

E.g. When 50cm^3 of 1.0M HNO_3 was neutralised by 50cm^3 of 1.0M NaOH the following results were obtained:

Starting temperature of solns. = 19.0°C

Maximum temperature reached = 25.1°C

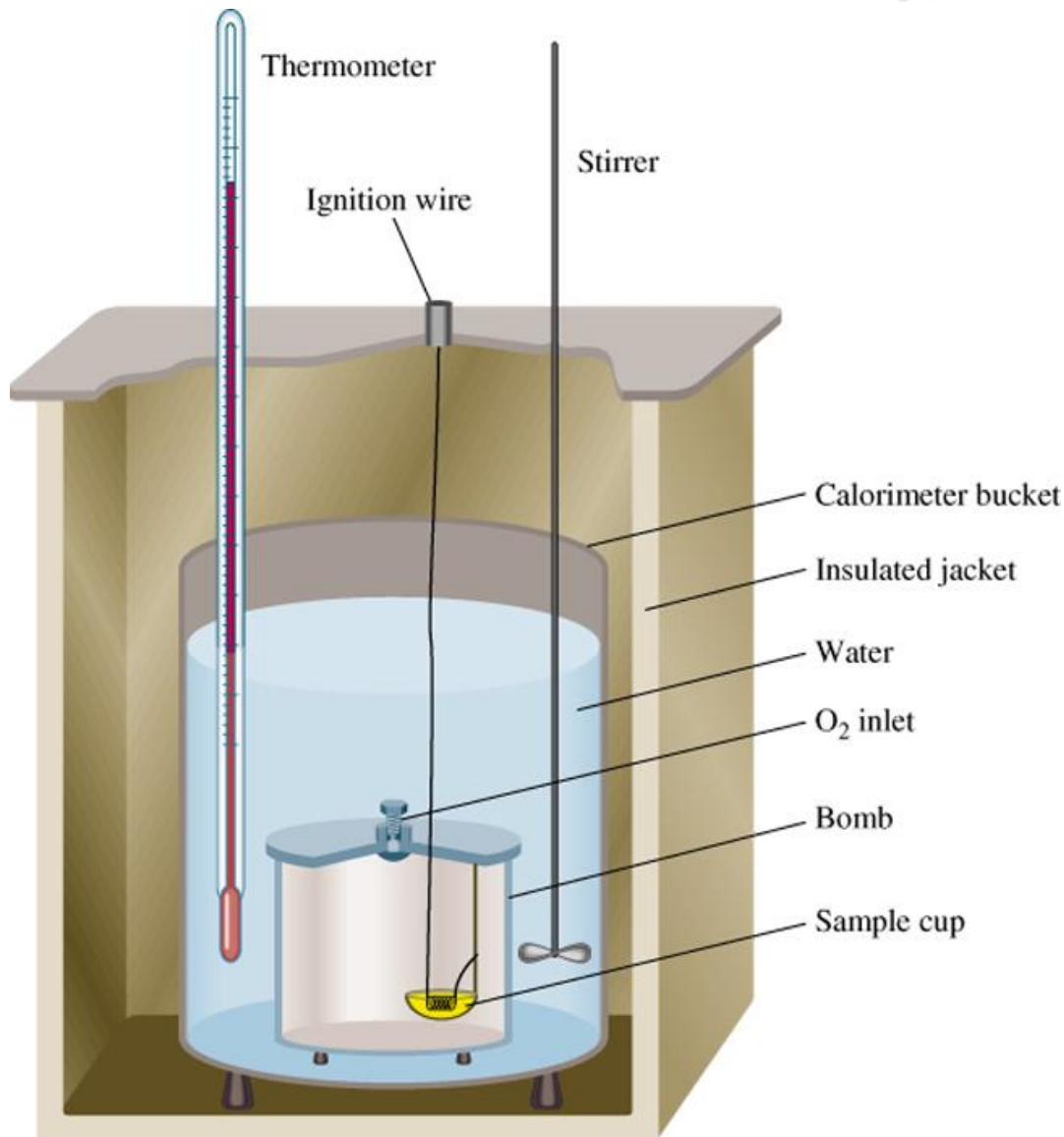
Calculate the heat absorbed by the solution, given that:

the mass of 1cm^3 of water = 1g ;

and that the specific heat capacity of water = $4.2 \text{ J K}^{-1} \text{g}^{-1}$.

$$q_p = m \times C_p \times \Delta T \quad q_p = 100 \times 4.2 \times 6.1 = 2562 \text{ J}$$

Constant-Volume Calorimetry



$$q_{\text{rxn}} = - (q_{\text{water}} + q_{\text{bomb}})$$

$$q_{\text{water}} = ms\Delta t$$

$$q_{\text{bomb}} = C_{\text{bomb}}\Delta t$$

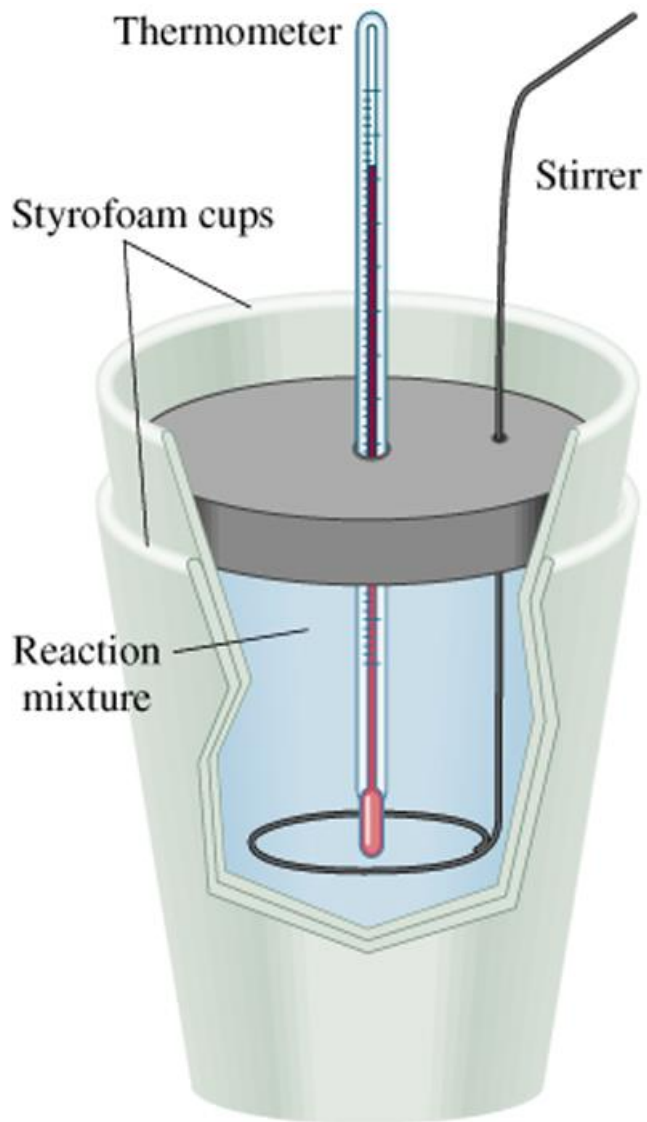
Reaction at Constant V

$$\Delta H \neq q_{\text{rxn}}$$

$$\Delta H \sim q_{\text{rxn}}$$

No heat enters or leaves!

Constant-Pressure Calorimetry



$$q_{\text{rxn}} = - (q_{\text{water}} + q_{\text{cal}})$$

$$q_{\text{water}} = ms\Delta t$$

$$q_{\text{cal}} = C_{\text{cal}}\Delta t$$

Reaction at Constant P

$$\Delta H = q_{\text{rxn}}$$

heat enters or leaves!

Table 6.2 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	56.2
Heat of fusion	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$	6.01
Heat of vaporization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	44.0*
Heat of reaction	$\text{MgCl}_2(s) + 2\text{Na}(l) \longrightarrow 2\text{NaCl}(s) + \text{Mg}(s)$	-180.2

* Measured at 25°C. At 100°C, the value is 40.79 kJ.



- Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?
- Establish an arbitrary scale with the **standard enthalpy of formation** ($\Delta_f H^0$) as a reference point for all enthalpy expressions.
- ***Standard enthalpy of formation*** ($\Delta_f H^0$) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.

- The standard enthalpy of formation of any element in its most stable form is zero.

$$\Delta_f H^0 (\text{O}_2) = 0$$

$$\Delta_f H^0 (\text{C, graphite}) = 0$$

$$\Delta_f H^0 (\text{O}_3) = 142 \text{ kJ/mol}$$

$$\Delta_f H^0 (\text{C, diamond}) = 1.90 \text{ kJ/mol}$$

Table 6.3 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
Ag(s)	0	H ₂ O ₂ (l)	-187.6
AgCl(s)	-127.04	Hg(l)	0
Al(s)	0	I ₂ (s)	0
Al ₂ O ₃ (s)	-1669.8	HI(g)	25.94
Br ₂ (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO ₃ (s)	-1112.9
C(diamond)	1.90	N ₂ (g)	0
CO(g)	-110.5	NH ₃ (g)	-46.3
CO ₂ (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO ₂ (g)	33.85
CaO(s)	-635.6	N ₂ O ₄ (g)	9.66
CaCO ₃ (s)	-1206.9	N ₂ O(g)	81.56
Cl ₂ (g)	0	O(g)	249.4
HCl(g)	-92.3	O ₂ (g)	0
Cu(s)	0	O ₃ (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F ₂ (g)	0	S(monoclinic)	0.30
HF(g)	-268.61	SO ₂ (g)	-296.1
H(g)	218.2	SO ₃ (g)	-395.2
H ₂ (g)	0	H ₂ S(g)	-20.15
H ₂ O(g)	-241.8	ZnO(s)	-347.98
H ₂ O(l)	-285.8		

Standard enthalpy change of...

Formation $\Delta_f H^\theta$ is the enthalpy change when 1 mole of a compound is made from its elements in their standard states, under standard conditions.

Combustion $\Delta_c H^\theta$ is the enthalpy change when 1 mole of a substance burns completely in oxygen, under standard conditions.

Atomisation $\Delta_{at} H^\theta$ is the enthalpy change when 1 mole of gaseous atoms is made from the element in its standard state, under standard conditions.

Standard enthalpy change of...

Reaction $\Delta_r H^\theta$ is the enthalpy change when **molar quantities of reactants as stated in an equation** react under standard conditions.

Neutralisation $\Delta_n H^\theta$ is the energy released when **unit molar quantities of acids and alkalis completely neutralise** each other at 298K.

Note: Make sure that you know these definitions

The **standard enthalpy of reaction** (ΔH_{rxn}^0) is the enthalpy of a reaction carried out at 1 atm.



$$\Delta H_{\text{rxn}}^0 = [c\Delta H_{\text{f}}^0 (\text{C}) + d\Delta H_{\text{f}}^0 (\text{D})] - [a\Delta H_{\text{f}}^0 (\text{A}) + b\Delta H_{\text{f}}^0 (\text{B})]$$

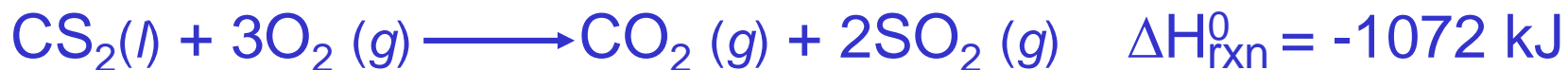
$$\Delta H_{\text{rxn}}^0 = \Sigma n\Delta H_{\text{f}}^0 (\text{products}) - \Sigma m\Delta H_{\text{f}}^0 (\text{reactants})$$

Hess's Law: When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

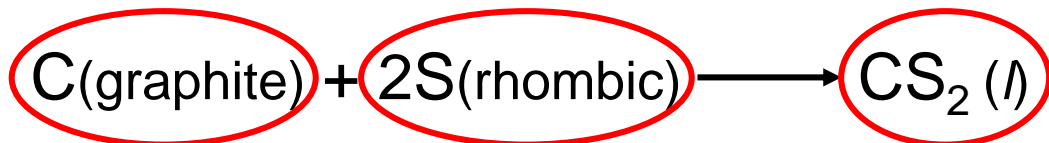
(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)



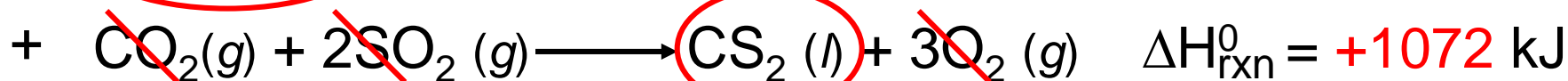
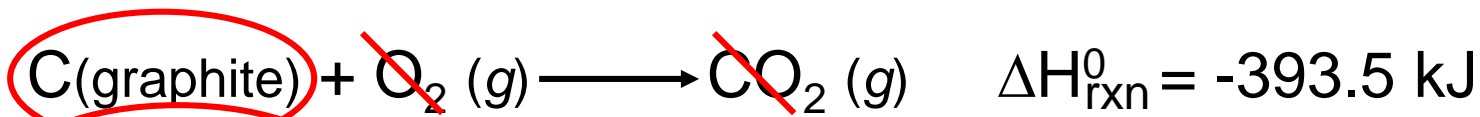
Calculate the standard enthalpy of formation of $\text{CS}_2(l)$ given that:



1. Write the enthalpy of formation reaction for CS_2



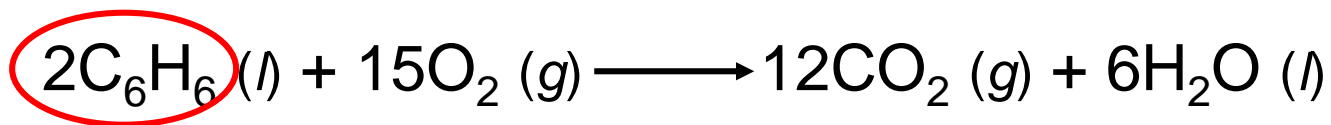
2. Add the given rxns so that the result is the desired rxn.



$$\Delta H_{\text{rxn}}^0 = -393.5 + (2 \times -296.1) + 1072 = 86.3 \text{ kJ}$$



Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.



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

$$\Delta H_{\text{rxn}}^0 = [12\Delta H_f^0(CO_2) + 6\Delta H_f^0(H_2O)] - [2\Delta H_f^0(C_6H_6)]$$

$$\Delta H_{\text{rxn}}^0 = [12 \times -393.5 + 6 \times -187.6] - [2 \times 49.04] = -5946 \text{ kJ}$$

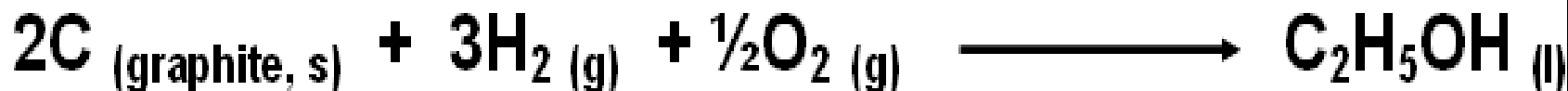
$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol } C_6H_6$$

Using enthalpy cycles

- Some enthalpy changes cannot be measured directly: e.g. The enthalpy of formation of ethanol

Standard Enthalpy of Formation, ΔH^{θ}_f is the enthalpy change when 1 mole of a compound is made from its elements in their standard states, under standard conditions.

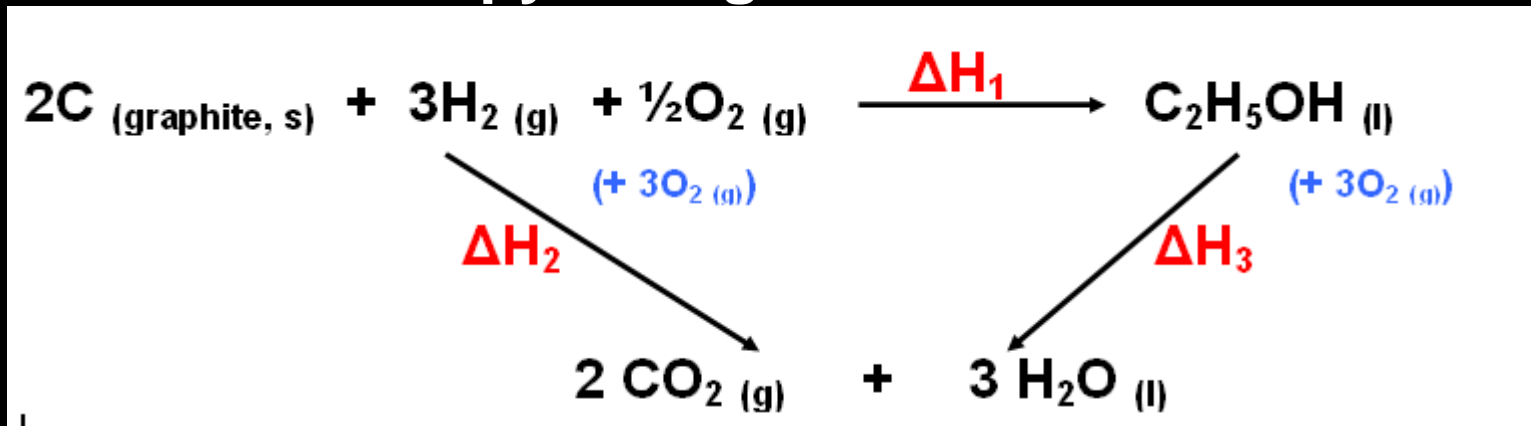
- Write the equation for the formation of ethanol from its elements.



- Why can't ethanol be prepared in this way?

Using enthalpy cycles to calculate enthalpy changes that cannot be measured directly

Although we cannot directly measure the enthalpy of formation of ethanol, it can be calculated by using other measurable enthalpy changes.

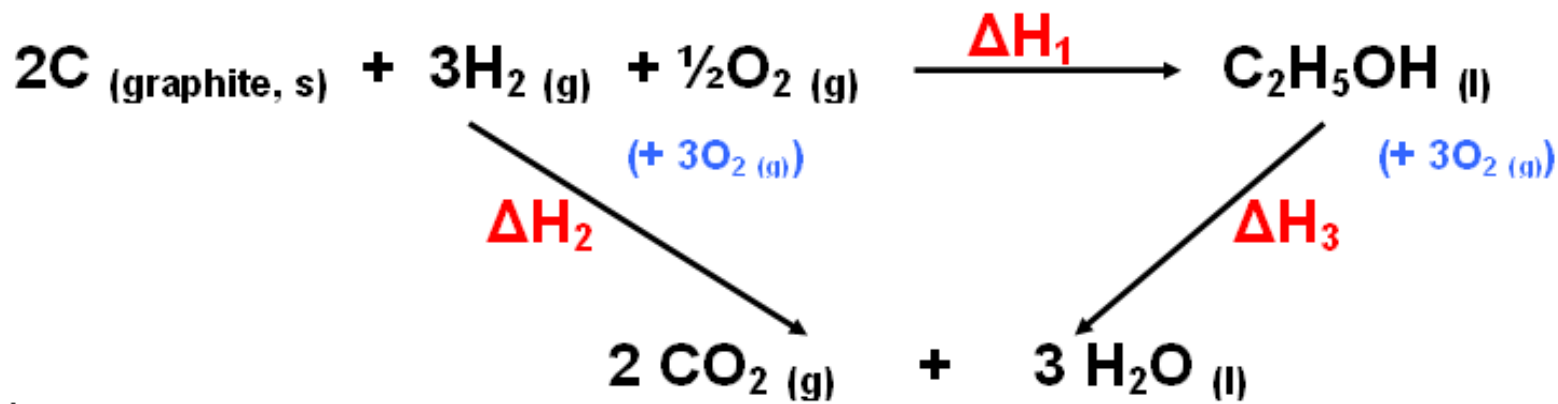


Where:

$\Delta H_1 = 2x$ (enthalpy of combustion of graphite) + $3x$ (enthalpy of combustion of hydrogen)

$\Delta H_3 =$ enthalpy of combustion of ethanol

Enthalpy of Formation of Ethanol



$$\Delta H_c^\ominus[\text{C, graphite(s)}] = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\ominus[\text{H}_2\text{(g)}] = -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H_c^\ominus[\text{C}_2\text{H}_5\text{OH(l)}] = -1367.3 \text{ kJ mol}^{-1}$$

Use the information above to calculate the enthalpy of formation of ethanol.

Calculating the heat of formation of ethanol

From the previous slide:

$$\Delta H_1 = \Delta H_2 - \Delta H_3$$



So:

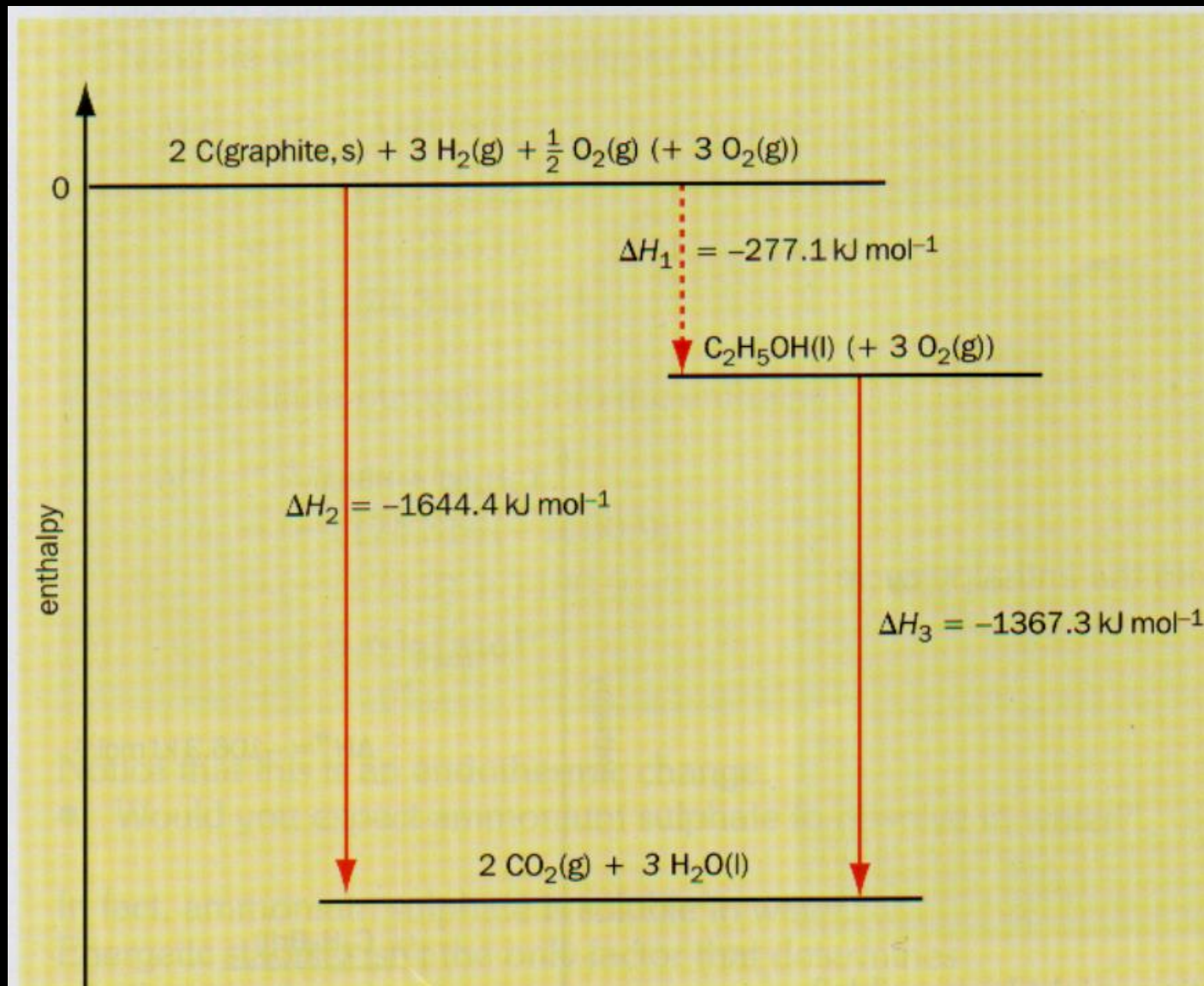
$$\Delta H_2 = 2\Delta H_c^\ominus[\text{C, graphite}_{(s)}] + 3\Delta H_c^\ominus[\text{H}_{2,(g)}]$$

$$\Delta H_3 = \Delta H_c^\ominus[\text{C}_2\text{H}_5\text{OH}_{(l)}]$$

$$\begin{aligned}\Delta H_1 &= \Delta H_2 - \Delta H_3 \\ &= [2(-393.5) + 3(-285.8)] - [-1367.3] \\ &= [-787 - 857.4] + 1367.3 \\ &= -1644.4 + 1367.3 \\ &= \underline{\underline{-277.4\text{kJmol}^{-1}}}\end{aligned}$$

Enthalpy Level Diagram

This is another way to show the enthalpy changes in an energy cycle:



The **enthalpy of solution** (ΔH_{soln}) is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

$$\Delta H_{\text{soln}} = H_{\text{soln}} - H_{\text{components}}$$

Table 6.4 Heats of Solution of Some Ionic Compounds

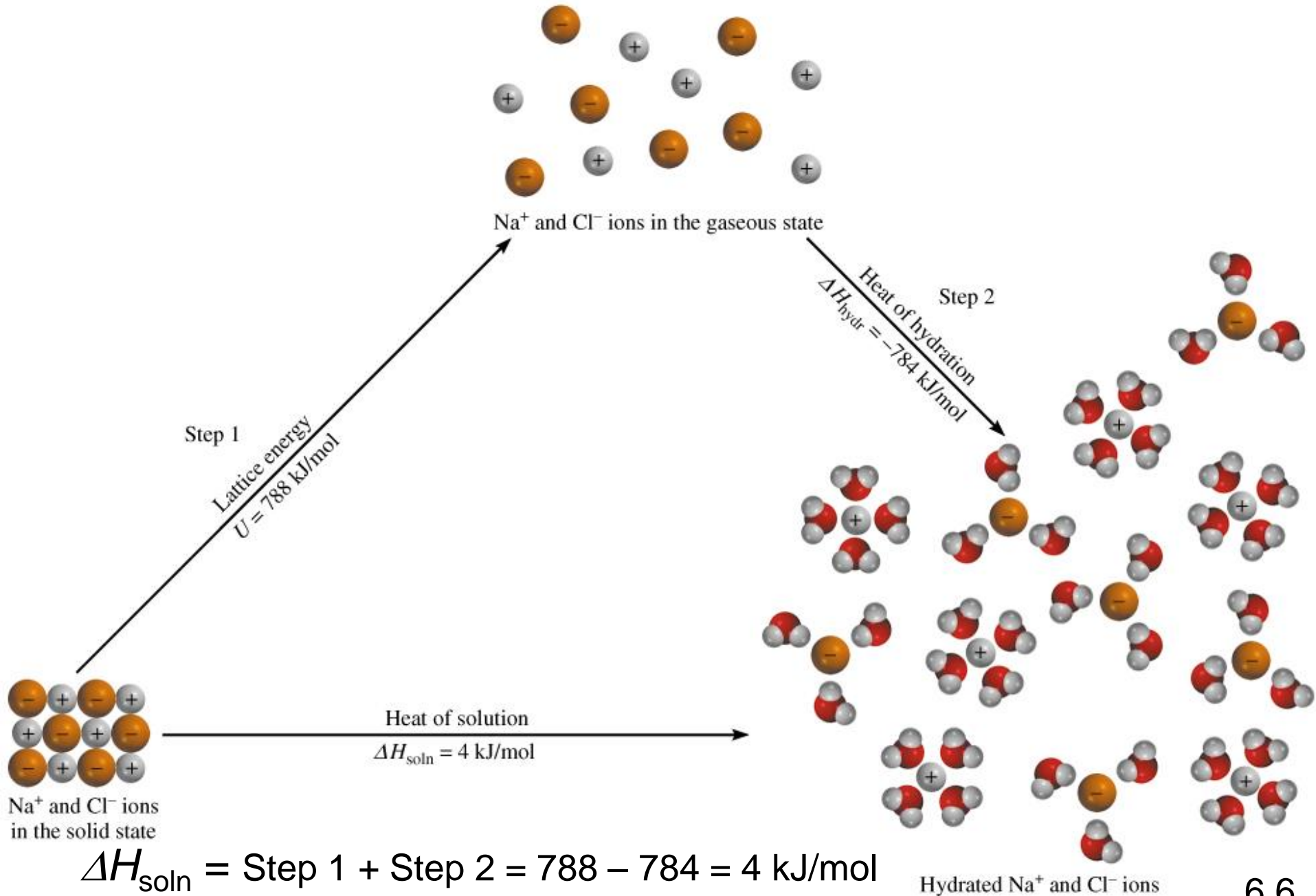
Compound	ΔH_{soln} (kJ/mol)	
LiCl	-37.1	} exothermic
CaCl ₂	-82.8	
NaCl	4.0	} endothermic
KCl	17.2	
NH ₄ Cl	15.2	
NH ₄ NO ₃	26.2	

Which substance(s) could be used for melting ice?

Which substance(s) could be used for a cold pack?

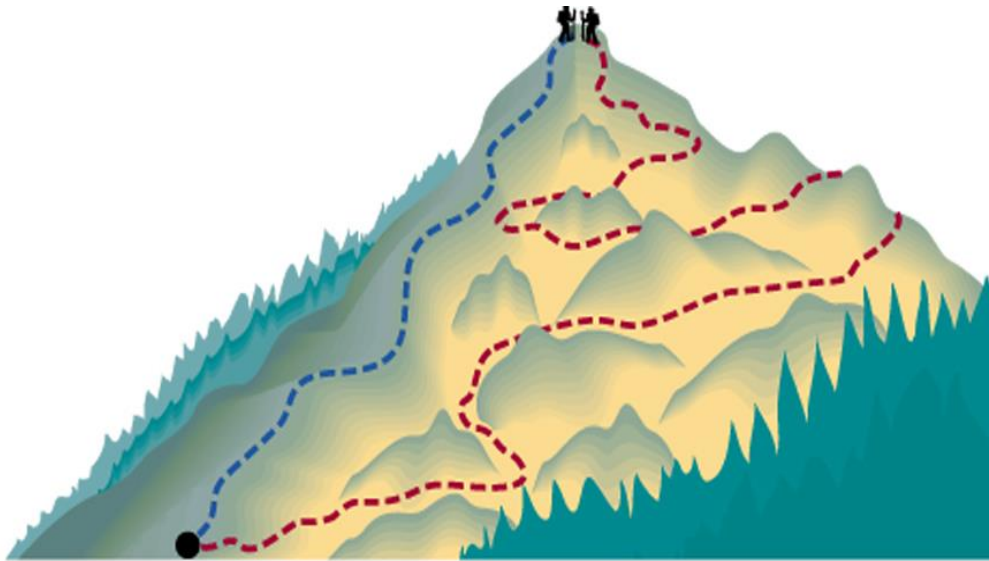
End

The Solution Process for NaCl



Thermodynamics

- **State functions** are properties that are determined by the state of the system, regardless of how that condition was achieved.



volume, temperature
energy , pressure

- Potential energy of **hiker 1** and **hiker 2** is the same even though they took different paths.

Thermodynamics

$$\Delta E = q + w$$

ΔE is the change in internal energy of a system

q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

$w = -P\Delta V$ when a gas expands against a constant external pressure

Table 6.5 Sign Conventions for Work and Heat

Process	Sign
Work done by the system on the surroundings	–
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	–

Enthalpy and the First Law of Thermodynamics

$$\Delta E = q + w$$

At constant pressure, $q = \Delta H$ and $w = -P\Delta V$

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

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

