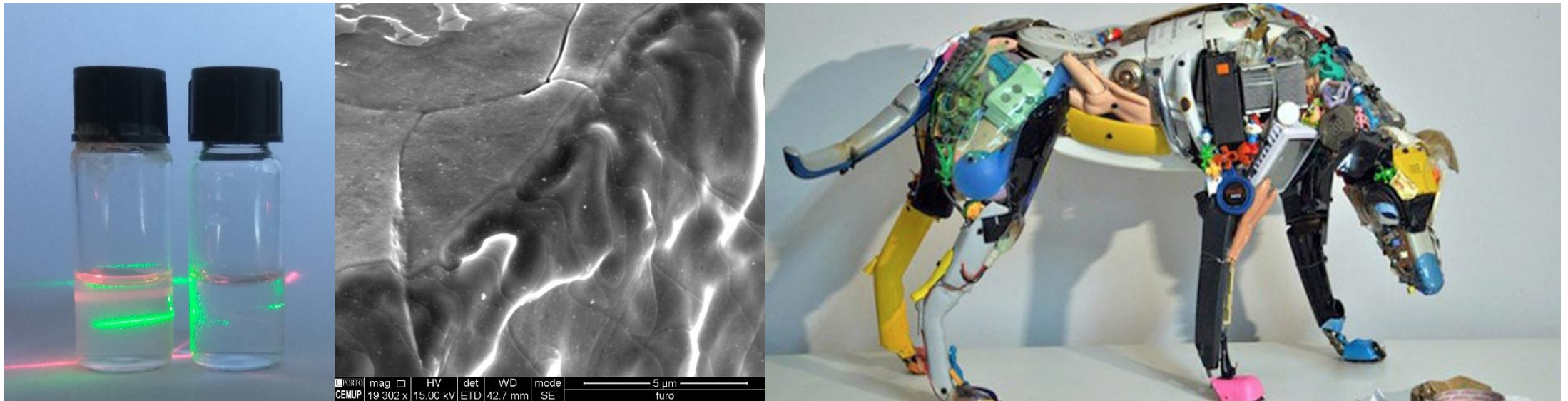


# Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.



## Thermochemistry

The study of the **energy transferred as heat** during the course of chemical reactions

Standard enthalpy change,  $\Delta H^\ominus$

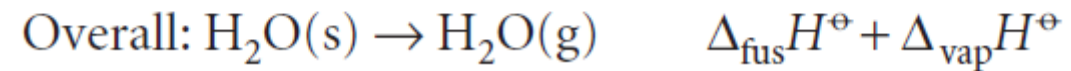
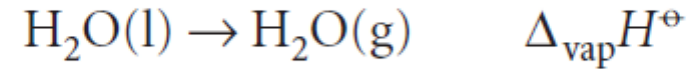
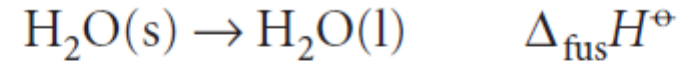
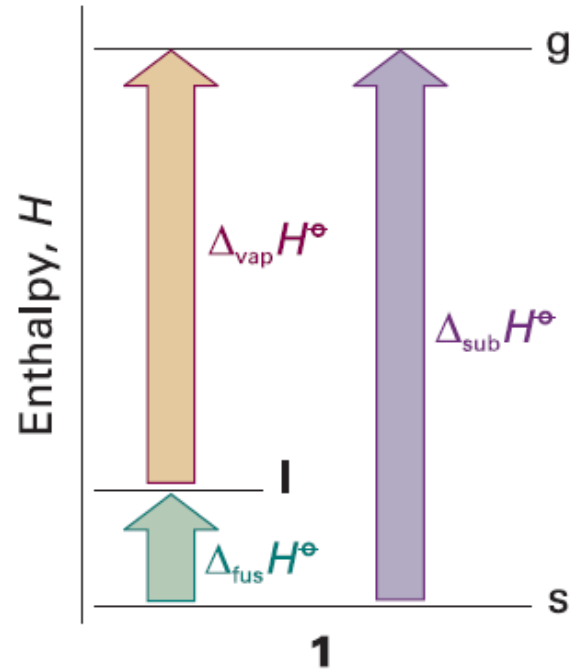
The **Standard State** of a substance at a specified temperature is its pure form at  $p^\ominus = 1$  bar.

As an example of a standard enthalpy change, the *standard enthalpy of vaporization*,  $\Delta_{\text{vap}}H^\ominus$ , is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar, as in



$$H(V, T, n)$$

## Thermochemistry

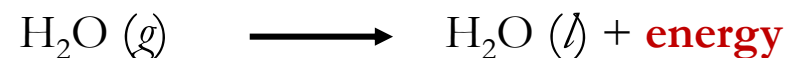


**Synoptic Table 2.3\*** Standard enthalpies of fusion and vaporization at the transition temperature,  $\Delta_{\text{trs}}H^\ominus/(\text{kJ mol}^{-1})$

	$T_f/\text{K}$	Fusion	$T_b/\text{K}$	Vaporization
Ar	83.81	1.188	87.29	6.506
$\text{C}_6\text{H}_6$	278.61	10.59	353.2	30.8
$\text{H}_2\text{O}$	273.15	6.008	373.15	40.656 (44.016 at 298 K)
He	3.5	0.021	4.22	0.084

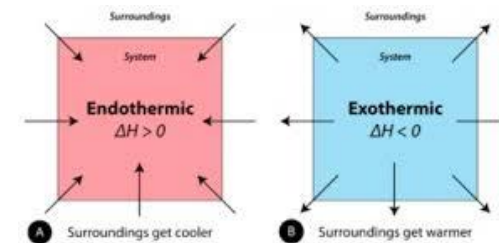
### Exothermic process

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



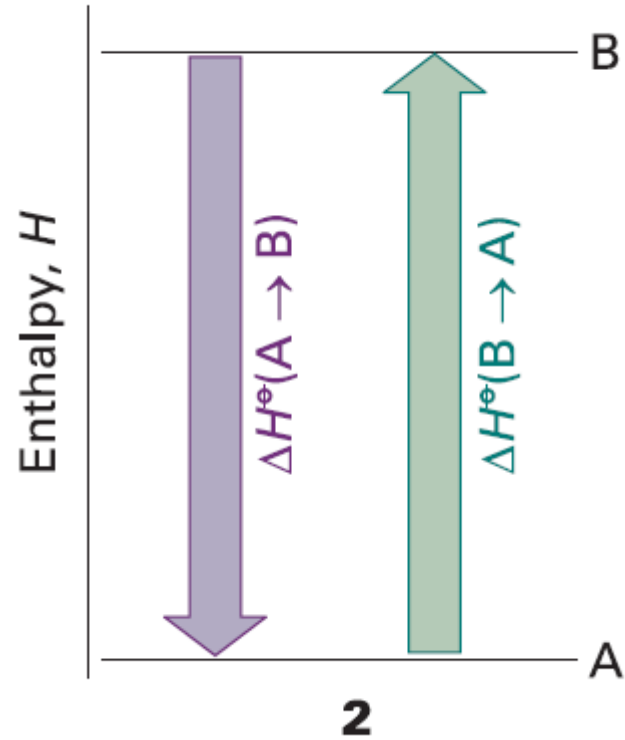
### Endothermic process

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



$$U(V, T, n)$$

## First Law of Thermodynamics



$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A)$$

Another consequence of  $H$  being a state function is that the standard enthalpy changes of a forward process and its reverse differ in sign (2):

$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A) \quad (2.31)$$

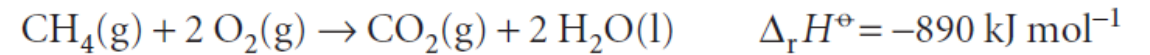
For instance, because the **enthalpy of vaporization** of water is  $+44 \text{ kJ mol}^{-1}$  at 298 K, its **enthalpy of condensation** at that temperature is  $-44 \text{ kJ mol}^{-1}$ .

**Table 2.4** Enthalpies of transition

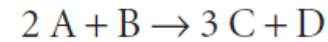
Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow$ phase $\beta$	$\Delta_{\text{trs}}H$
Fusion	$s \rightarrow l$	$\Delta_{\text{fus}}H$
Vaporization	$l \rightarrow g$	$\Delta_{\text{vap}}H$
Sublimation	$s \rightarrow g$	$\Delta_{\text{sub}}H$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{\text{mix}}H$
Solution	Solute $\rightarrow$ solution	$\Delta_{\text{sol}}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{\text{hyd}}H$
Atomization	Species(s, l, g) $\rightarrow$ atoms(g)	$\Delta_{\text{at}}H$
Ionization	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_{\text{ion}}H$
Electron gain	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{\text{eg}}H$
Reaction	Reactants $\rightarrow$ products	$\Delta_r H$
Combustion	Compounds(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_c H$
Formation	Elements $\rightarrow$ compound	$\Delta_f H$
Activation	Reactants $\rightarrow$ activated complex	$\Delta^\ddagger H$

\* IUPAC recommendations. In common usage, the transition subscript is often attached to  $\Delta H$ , as in  $\Delta H_{\text{trs}}$ .

## Standard Reaction Enthalpy $\Delta_r H^\ominus$



For the reaction

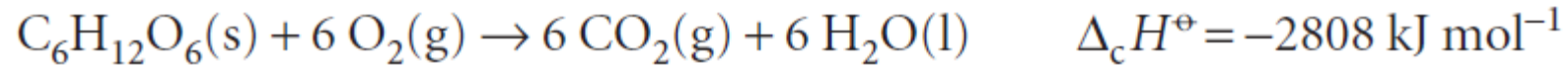


$$\Delta_r H^\ominus = \{3H_m^\ominus(\text{C}) + H_m^\ominus(\text{D})\} - \{2H_m^\ominus(\text{A}) + H_m^\ominus(\text{B})\}$$

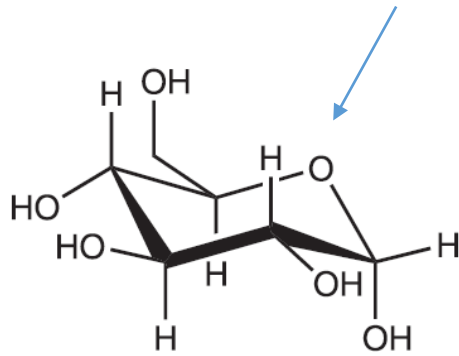
$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus$$

Pure, separate reactants in their standard states  
 $\rightarrow$  pure, separate products in their standard states

Standard Enthalpy of Combustion  $\Delta_c H^\ominus$



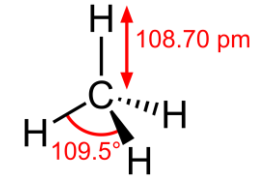
*Specific enthalpy*



**glucose**

**Table 2.6** Thermochemical properties of some fuels

Fuel	Combustion equation	$\Delta_c H^\ominus /$ (kJ mol <sup>-1</sup> )	Specific enthalpy/ (kJ g <sup>-1</sup> )	Enthalpy density/ (kJ dm <sup>-3</sup> )
Hydrogen	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-286	142	13
Methane	$\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	-890	55	40
Octane	$\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2} \text{O}_2(\text{g}) \rightarrow 8 \text{CO}_2(\text{g}) + 9 \text{H}_2\text{O}(\text{l})$	-5471	48	$3.8 \times 10^4$
Methanol	$\text{CH}_3\text{OH}(\text{l}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	-726	23	$1.8 \times 10^4$



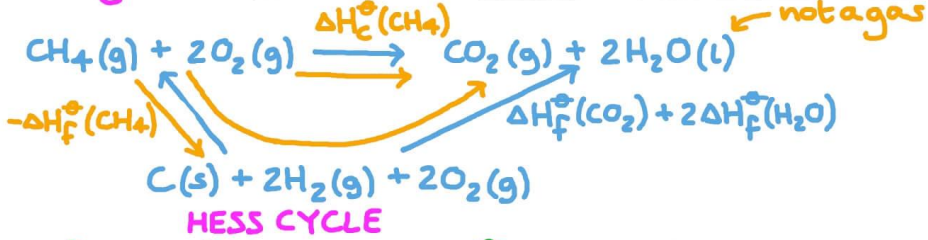
Chemical **ENERGY** or **Enthalpy** change of a substance,

Using the data in the table, calculate to the nearest kJ/mol the standard enthalpy of combustion of methane.

*graphite*  $C(s) + 2H_2(g) \rightarrow CH_4(g)$  *standard state*

Substance	$CH_4(g)$	$CO_2(g)$	$H_2O(l)$	$O_2(g)$
$\Delta H_f^\ominus$ (kJ/mol)	-74.6	-393.51	-285.83	0

*standard combustion*  $\Delta H_c^\ominus$  *enthalpy change*



$$\Delta H_c^\ominus = \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants})$$

$$\Delta H_c^\ominus(CH_4) = -\Delta H_f^\ominus(CH_4) + \Delta H_f^\ominus(CO_2) + 2\Delta H_f^\ominus(H_2O)$$

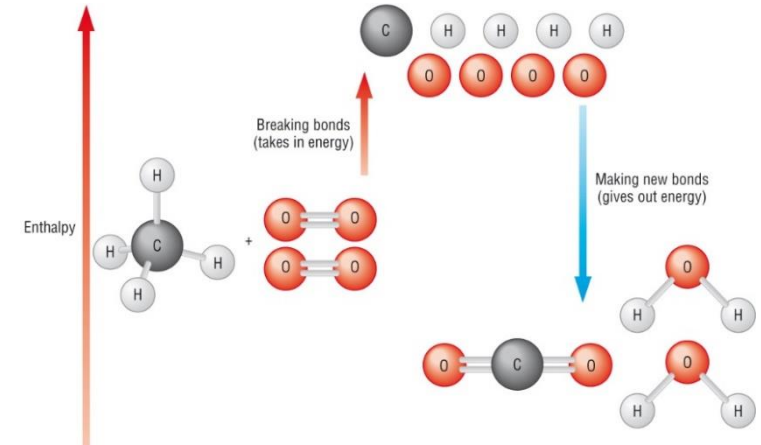
$$= -(-74.6) + (-393.51) + 2(-285.83)$$

$$= 74.6 - 393.51 - 571.66$$

$$= -890.57 \text{ kJ/mol} = \boxed{-891 \text{ kJ/mol}} \text{ (exothermic)}$$

*891 kJ*

$H_2O$   
 $CO_2$   
 $H_2O$

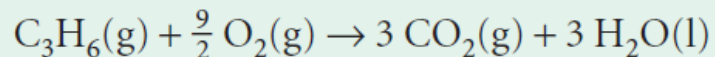




## Hess's law

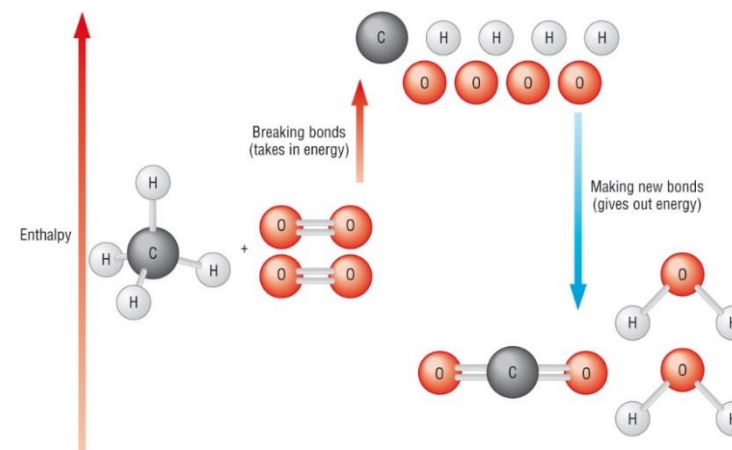
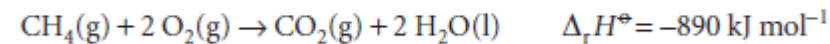
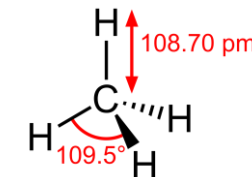
The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

This application of the **First Law**



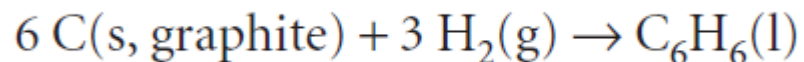
This reaction can be recreated from the following sum:

	$\Delta_r H^\ominus / (\text{kJ mol}^{-1})$
$\text{C}_3\text{H}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$	-124
$\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$	-2220
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$	+286
<hr/>	
$\text{C}_3\text{H}_6(\text{g}) + \frac{9}{2} \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$	-2058



Standard Enthalpies of Formation  $\Delta_f H^\ominus$ 

The standard **reaction enthalpy for the formation** of the compound from its elements in their reference states



benzene

**Reference State** of an element is its most stable state at the specified temperature and 1 bar.

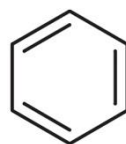
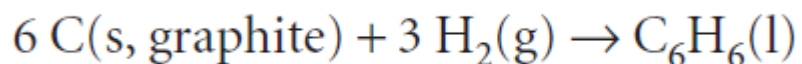
**Synoptic Table 2.7\*** Standard enthalpies of formation of inorganic compounds at 298 K

	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$
$\text{H}_2\text{O}(\text{l})$	-285.83
$\text{H}_2\text{O}(\text{g})$	-187.78
$\text{NH}_3(\text{g})$	-46.11
$\text{N}_2\text{H}_4(\text{l})$	+50.63
$\text{NO}_2(\text{g})$	33.18
$\text{N}_2\text{O}_4(\text{g})$	+9.16
$\text{NaCl}(\text{s})$	-411.15
$\text{KCl}(\text{s})$	-436.75

## Standard Enthalpies of Formation

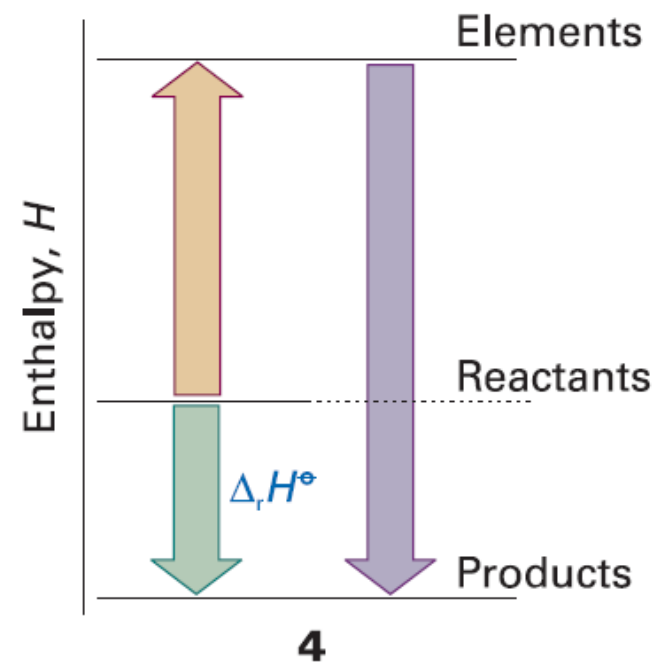
$$\Delta_f H^\ominus$$

The standard **reaction enthalpy for the formation** of the compound from its elements in their reference states



benzene

**Reference State** of an element is its most stable state at the specified temperature and 1 bar.



## Standard enthalpies of formation

$$\Delta_f H^\ominus$$

The standard enthalpy of **formation of ions in solution** poses a special problem because it is impossible to prepare a solution of cations alone or of anions alone

$$\Delta_f H^\ominus(\text{H}^+, \text{aq}) = 0$$

**conventionally** the hydrogen ion (zero)

e.g.

HBr(aq) is found to be  $-122 \text{ kJ mol}^{-1}$

$$\Delta_f H^\ominus(\text{Br}^-, \text{aq}) = -122 \text{ kJ mol}^{-1}$$

**Synoptic Table 2.7\*** Standard enthalpies of formation of inorganic compounds at 298 K

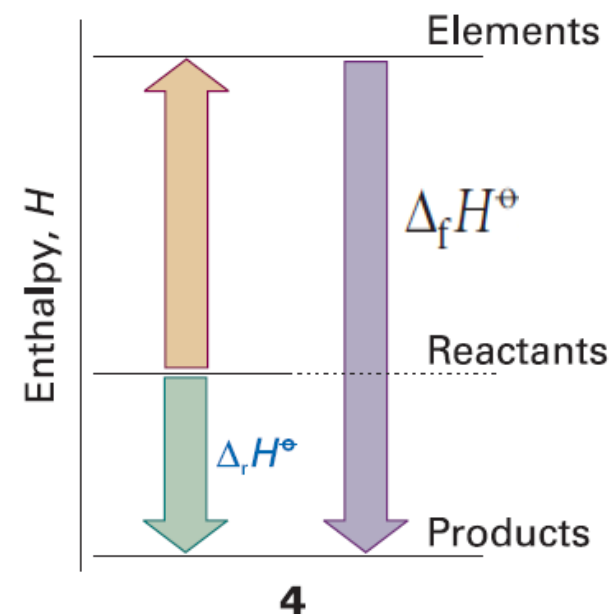
	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$
H <sub>2</sub> O(l)	-285.83
H <sub>2</sub> O(g)	-187.78
NH <sub>3</sub> (g)	-46.11
N <sub>2</sub> H <sub>4</sub> (l)	+50.63
NO <sub>2</sub> (g)	33.18
N <sub>2</sub> O <sub>4</sub> (g)	+9.16
NaCl(s)	-411.15
KCl(s)	-436.75

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus$$

### Illustration 2.7 Using standard enthalpies of formation

The standard reaction enthalpy of  $2 \text{HN}_3(\text{l}) + 2 \text{NO}(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) + 4 \text{N}_2(\text{g})$  is calculated as follows:

$$\begin{aligned} \Delta_r H^\ominus &= \{\Delta_f H^\ominus(\text{H}_2\text{O}_2, \text{l}) + 4\Delta_f H^\ominus(\text{N}_2, \text{g})\} - \{2\Delta_f H^\ominus(\text{HN}_3, \text{l}) + 2\Delta_f H^\ominus(\text{NO}, \text{g})\} \\ &= \{-187.78 + 4(0)\} \text{ kJ mol}^{-1} - \{2(264.0) + 2(90.25)\} \text{ kJ mol}^{-1} \\ &= -896.3 \text{ kJ mol}^{-1} \end{aligned}$$

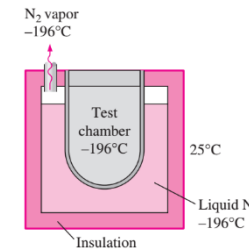


$$H(V, T, n)$$

Thermochemistry

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

Substance is heated from  $T_1$  to  $T_2$



Heat capacity at constant pressure

T1

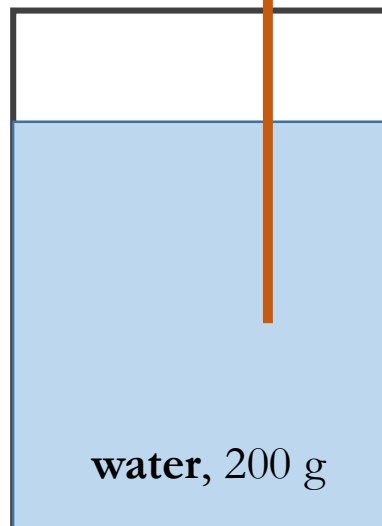


Copper, 50 g

$$T_1 = 50.0 \text{ } ^\circ\text{C}$$

$$C_p = 0.381 \text{ J g}^{-1} \text{ K}^{-1}$$

T2

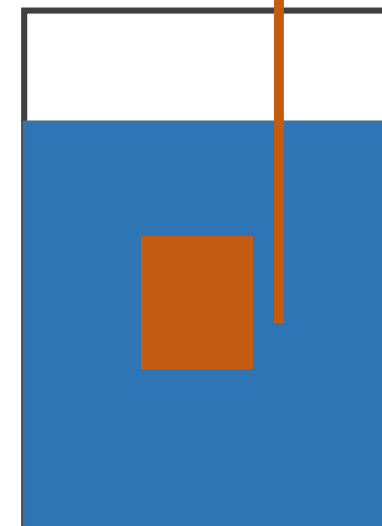


water, 200 g

$$T_2 = 22.0 \text{ } ^\circ\text{C}$$

$$C_p = 4.814 \text{ J g}^{-1} \text{ K}^{-1}$$

T3



$$T_3 = ??? \text{ } ^\circ\text{C}$$

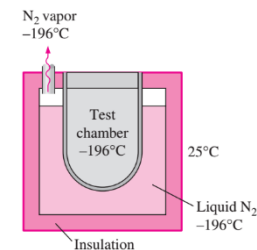
$$H(V, T, n)$$

Thermochemistry

Heat capacity at constant pressure

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

Substance is heated from  $T_1$  to  $T_2$

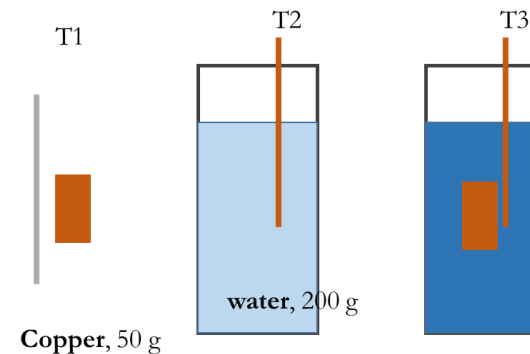


Process A

EXOthermic

Copper, 50 g       $T_1 = 50.0 \text{ }^\circ\text{C}$        $\longrightarrow$        $T_3 = ??? \text{ }^\circ\text{C}$

$$Q_A = \text{Mass}(\text{Cu}) \times C_p(\text{Cu}) \times (T_3 - T_1) = 50.0 \times 0.381 \times (T_3 - 50.0)$$



Process B

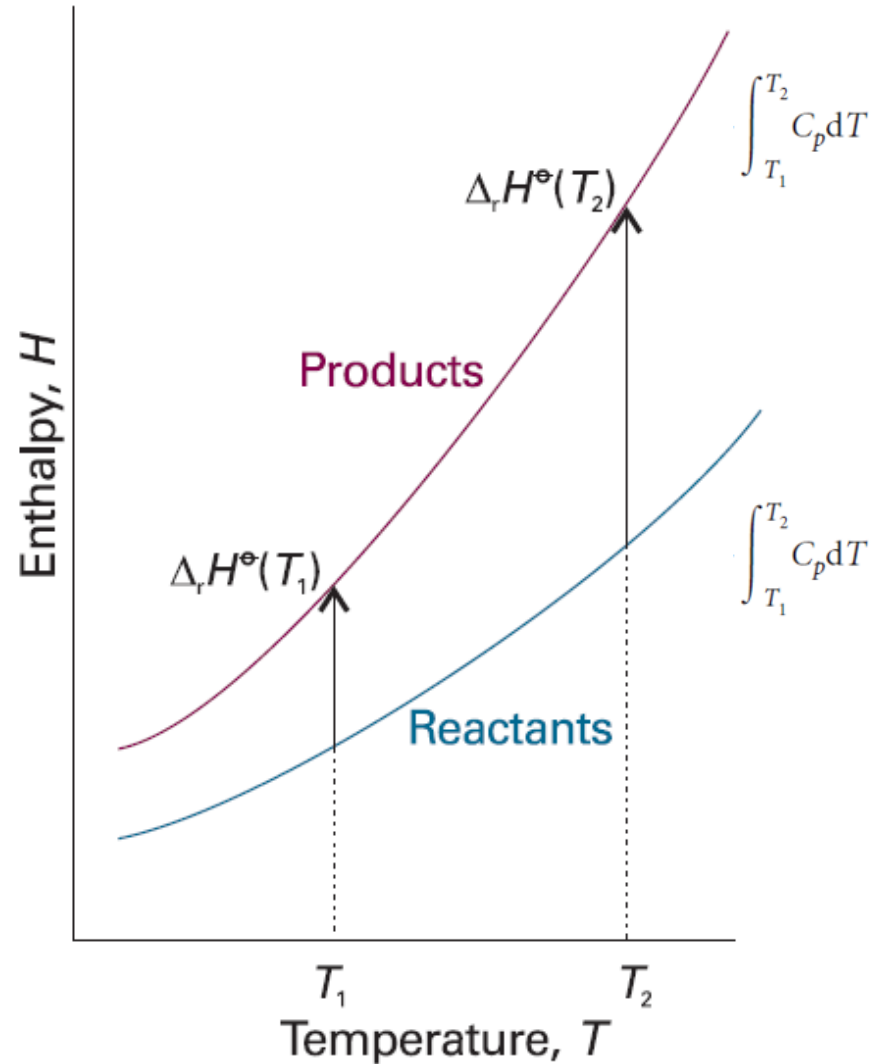
ENDOthermic

Water, 200 g       $T_2 = 22.0 \text{ }^\circ\text{C}$        $\longrightarrow$        $T_3 = ??? \text{ }^\circ\text{C}$

$$Q_B = \text{Mass}(\text{H}_2\text{O}) \times C_p(\text{H}_2\text{O}) \times (T_3 - T_2) = 200 \times 4.814 \times (T_3 - 22.0)$$

$$Q_A + Q_B = 0$$

**R:**  $T_3 = 22.5 \text{ }^\circ\text{C}$



$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

Substance is heated from  $T_1$  to  $T_2$

Kirchhoff's law

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu C_{p,m}^\ominus$$

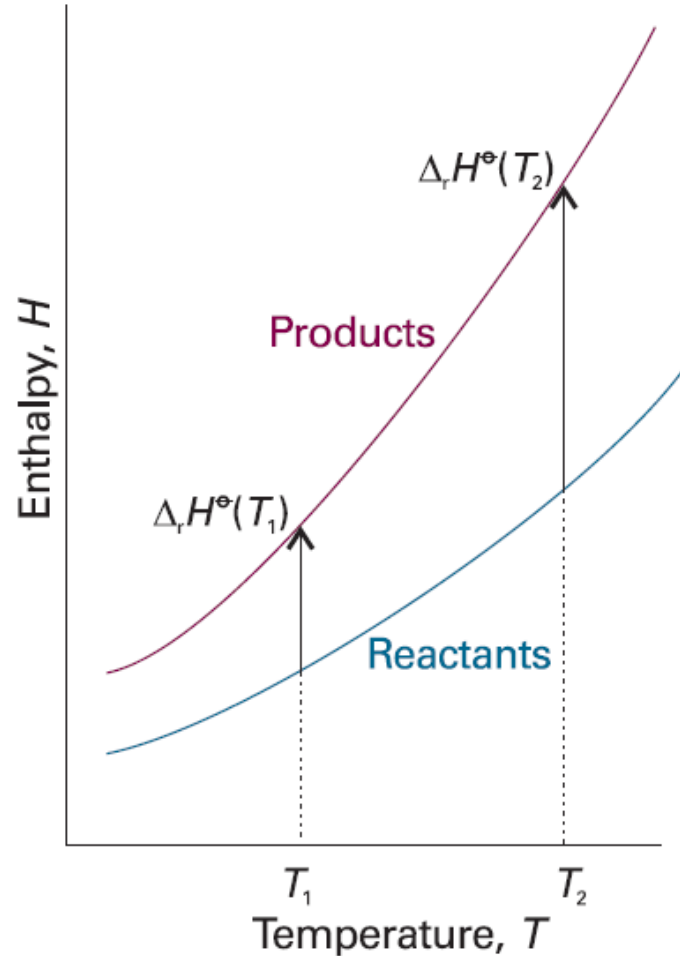


$$H(V, T, n)$$

Thermochemistry

Kirchhoff's law

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$



The standard enthalpy of formation of gaseous H<sub>2</sub>O at 298 K is −241.82 kJ mol<sup>−1</sup>. Estimate its value at 100°C given the following values of the molar heat capacities at constant pressure: H<sub>2</sub>O(g): 33.58 J K<sup>−1</sup> mol<sup>−1</sup>; H<sub>2</sub>(g): 28.84 J K<sup>−1</sup> mol<sup>−1</sup>; O<sub>2</sub>(g): 29.37 J K<sup>−1</sup> mol<sup>−1</sup>. Assume that the heat capacities are independent of temperature.

**Method** When  $\Delta C_p^\ominus$  is independent of temperature in the range  $T_1$  to  $T_2$ , the integral in eqn 2.36 evaluates to  $(T_2 - T_1)\Delta_r C_p^\ominus$ . Therefore,

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + (T_2 - T_1)\Delta_r C_p^\ominus$$

To proceed, write the chemical equation, identify the stoichiometric coefficients, and calculate  $\Delta_r C_p^\ominus$  from the data.

**Answer** The reaction is  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$ , so

$$\Delta_r C_p^\ominus = C_{p,m}^\ominus(\text{H}_2\text{O}, \text{g}) - \{C_{p,m}^\ominus(\text{H}_2, \text{g}) + \frac{1}{2}C_{p,m}^\ominus(\text{O}_2, \text{g})\} = -9.94 \text{ J K}^{-1} \text{ mol}^{-1}$$

It then follows that

$$\Delta_f H^\ominus(373 \text{ K}) = -241.82 \text{ kJ mol}^{-1} + (75 \text{ K}) \times (-9.94 \text{ J K}^{-1} \text{ mol}^{-1}) = -242.6 \text{ kJ mol}^{-1}$$

### Hess's law

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus$$

### Kirchhoff's law

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu C_{p,m}^\ominus$$

