Chemical Thermodynamics

Thermochemistry

Recommended books

1. P. W. Atkins and J. D. Paula: Physical Chemistry (10th edition)
2. Ira N. Levine: Physical Chemistry (6th edition)
3. M. Mahbubul Huque and M. Yousuf Ali Mollah: Principles of Physical Chemistry

Thermochemistry (7 lectures):
Standard states; thermochemical equations; enthalpy of reaction; Kirchhoff's equation; laws of thermochemistry; calorimetric measurements of bond activity and energies, enthalpy of reactions, formation, combustion, neutralization, solutions, dilution, fusion, vaporization, sublimation, hydrogenation.

Learning Outcomes (LOs)

Students should be able to:

a) Evaluate enthalpy change
b) Follow the latest sign convention for q, ΔU and w
c) Differentiate between exothermic and endothermic reactions
d) Define a thermochemical equation
e) Identify factors influencing heat of reaction
f) Evaluate heat of combustion and calorific value of foods and fuels
g) Define standard state
h) Follow enthalpy of formation and standard enthalpy of formation
i) Define enthalpy of neutralization, enthalpy of solution, enthalpy of hydration, enthalpy of fusion, enthalpy of vaporization, enthalpy of sublimation and lattice enthalpy
j) Define and understand Hess's law of constant heat summation
k) Define and calculate bond enthalpy
l) Explain the variation of heat of reaction with temperature (Kirchhoff's equation)

Lecture-1

Contents

- Thermochemistry
- Relation between q, ΔU and ΔH
- Exothermic and Endothermic processes
- Thermochemical Equation
- Standard states of pure substances

Thermochemistry

The study of the energy transferred as heat during the course of chemical reactions is called thermochemistry.

Thermochemistry is the branch of thermodynamics which deals with the thermal or heat changes caused by chemical reactions.

Relation of q with ΔU and ΔH

- We can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q.
- q indicates change in internal energy (ΔU) if the reaction occurs at constant volume.
- It indicates change in enthalpy (ΔH) if the reaction occurs at constant pressure.
- If we know ΔU or ΔH for a reaction, we can predict the heat the reaction can produce.

Exothermic and Endothermic Process

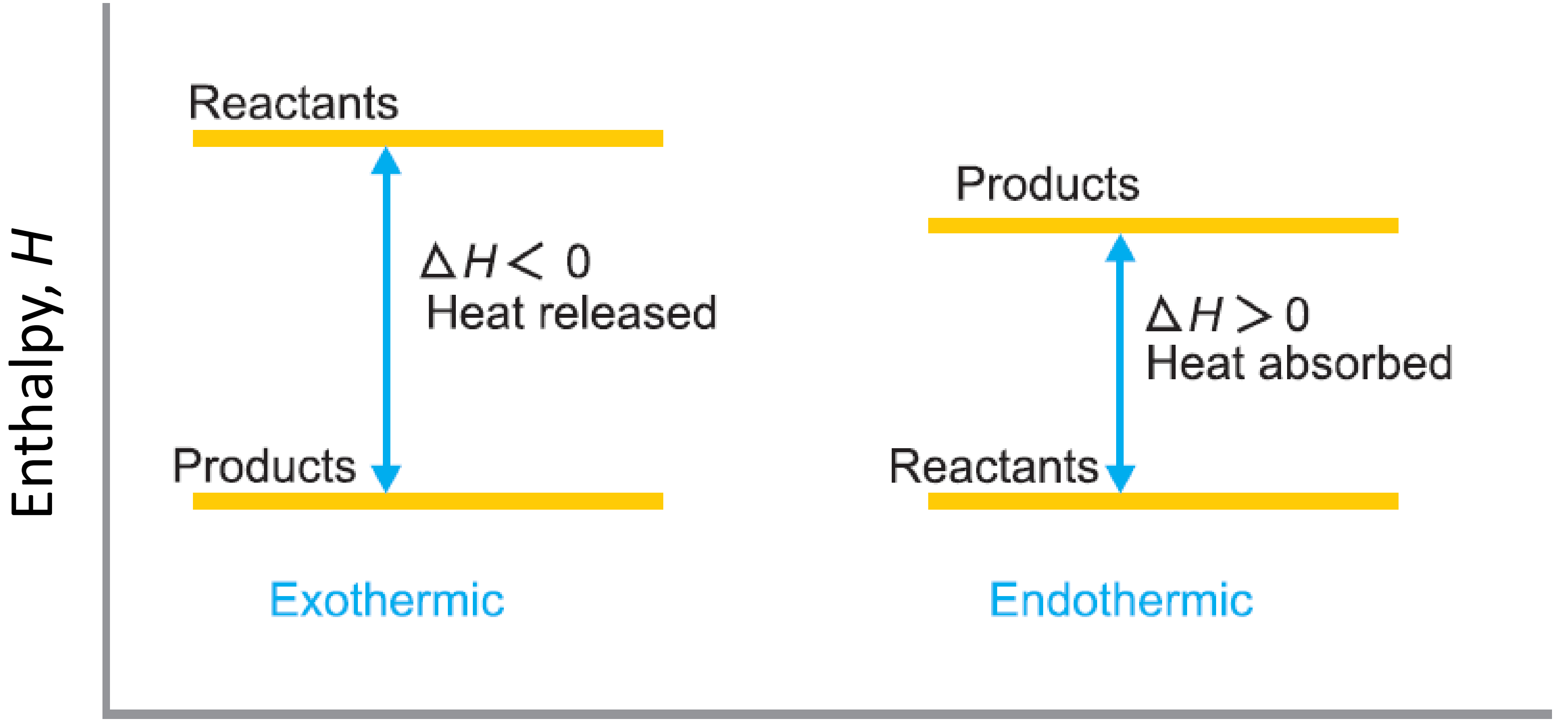
- A process that releases energy as heat into the surroundings is classified as exothermic.

  Exothermic process: $\Delta H < 0$

- A process that absorbs energy as heat from the surroundings is classified as endothermic.

  Endothermic process: $\Delta H > 0$

Enthalpy Diagram for Exothermic and Endothermic Reactions



Examples of Exothermic and Endothermic Processes

Exothermic Process	Endothermic Process
Making ice cubes	Melting ice cubes
Formation of snow in clouds	Conversion of frost to water vapour
Forming ion pairs	Separating ion pairs
Mixing water with an anhydrous salt	Making an anhydrous salt from a hydrated salt

Thermochemical Equation

A combination of a chemical equation and the corresponding change in standard enthalpy is called a thermochemical equation.

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) \quad \Delta H^{\ominus} = -890\,\text{kJ}$$

$\Delta H^{\ominus}$ is the change in enthalpy when reactants in their standard states change to products in their standard states

Standard states of pure substances

For a pure solid or a pure liquid, the standard state is defined as the state with pressure P = 1 bar and temperature T, where T is some temperature of interest.

Thus for each value of T there is a single standard state for a pure substance.

The symbol for a standard state is a degree superscript (read as “naught,” “zero,” or “standard”), with the temperature written as a subscript. For example, the molar volume of a pure solid or liquid at 1 bar and 200 K is symbolized by $V^\circ_{\mathrm{m},200}$.

Standard states of pure substances

- For a pure gas, the standard state at temperature T is chosen as the state where P = 1 bar and the gas behaves as an ideal gas.
- Since real gases do not behave ideally at 1 bar, the standard state of a pure gas is a fictitious state. Properties of the gas in the fictitious standard state are calculated from properties of the real gas.

Standard states of pure substances

Summary

- The standard states for pure substances are: Solid or liquid: P 1 bar, T
- Gas: $P = 1$ bar, T, gas ideal
- The standard-state pressure is denoted by $P°$:

$$P° = 1 \text{ bar}$$

Lecture-2

Contents

- Standard enthalpy of reaction
- Enthalpies of physical changes
- Enthalpies of chemical changes

Standard enthalpy of reaction

- The **standard enthalpy (change) of reaction** $\Delta H°_T$ for a chemical reaction is defined as the enthalpy change for the process of transforming stoichiometric numbers of moles of the pure, separated reactants, each in its standard state at temperature T, to stoichiometric numbers of moles of the pure, separated products, each in its standard state at the same temperature T.
- Often $\Delta H°_T$ or $\Delta_r H°_T$ is called the *heat of reaction.*
- The quantity $\Delta U°_T$ is defined in a similar manner.

Standard enthalpy of reaction

For the reaction

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$$

the standard enthalpy change ΔH°_T is

$$\Delta H^\circ_T \equiv cH^\circ_{\mathrm{m},T}(\mathrm{C}) + dH^\circ_{\mathrm{m},T}(\mathrm{D}) - aH^\circ_{\mathrm{m},T}(\mathrm{A}) - bH^\circ_{\mathrm{m},T}(\mathrm{B})$$

where $\Delta H^\circ_{\mathrm{m},T}(\mathrm{C})$ is the molar enthalpy of substance C in its standard state at temperature T.

Enthalpies of physical change

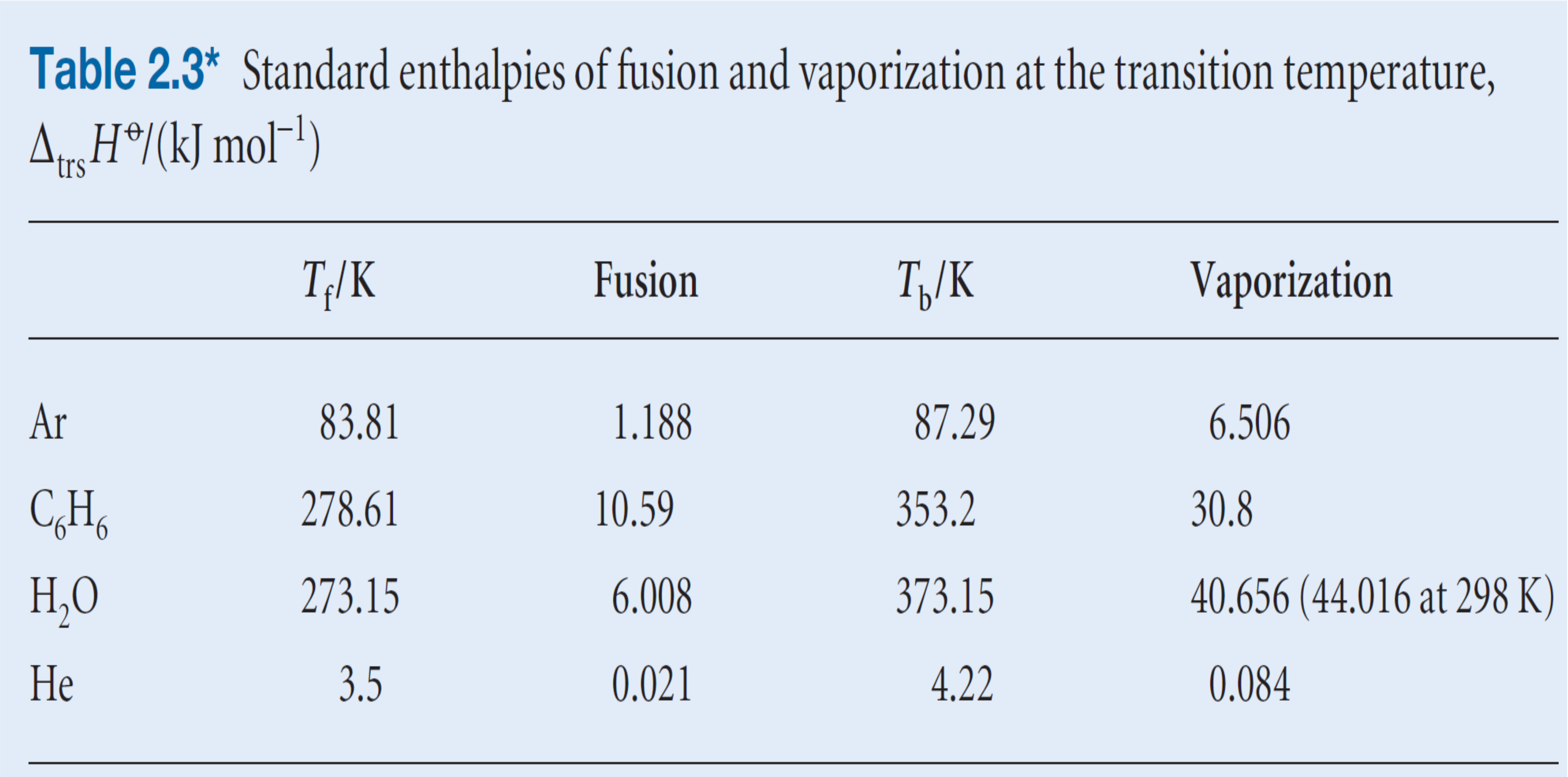


Table 2.3* Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{trs}H^{\ominus}/(\mathrm{kJ\ mol^{-1}})$

	T_f/K	Fusion	T_b/K	Vaporization
Ar	83.81	1.188	87.29	6.506
C_6H_6	278.61	10.59	353.2	30.8
H_2O	273.15	6.008	373.15	40.656 (44.016 at 298 K)
He	3.5	0.021	4.22	0.084

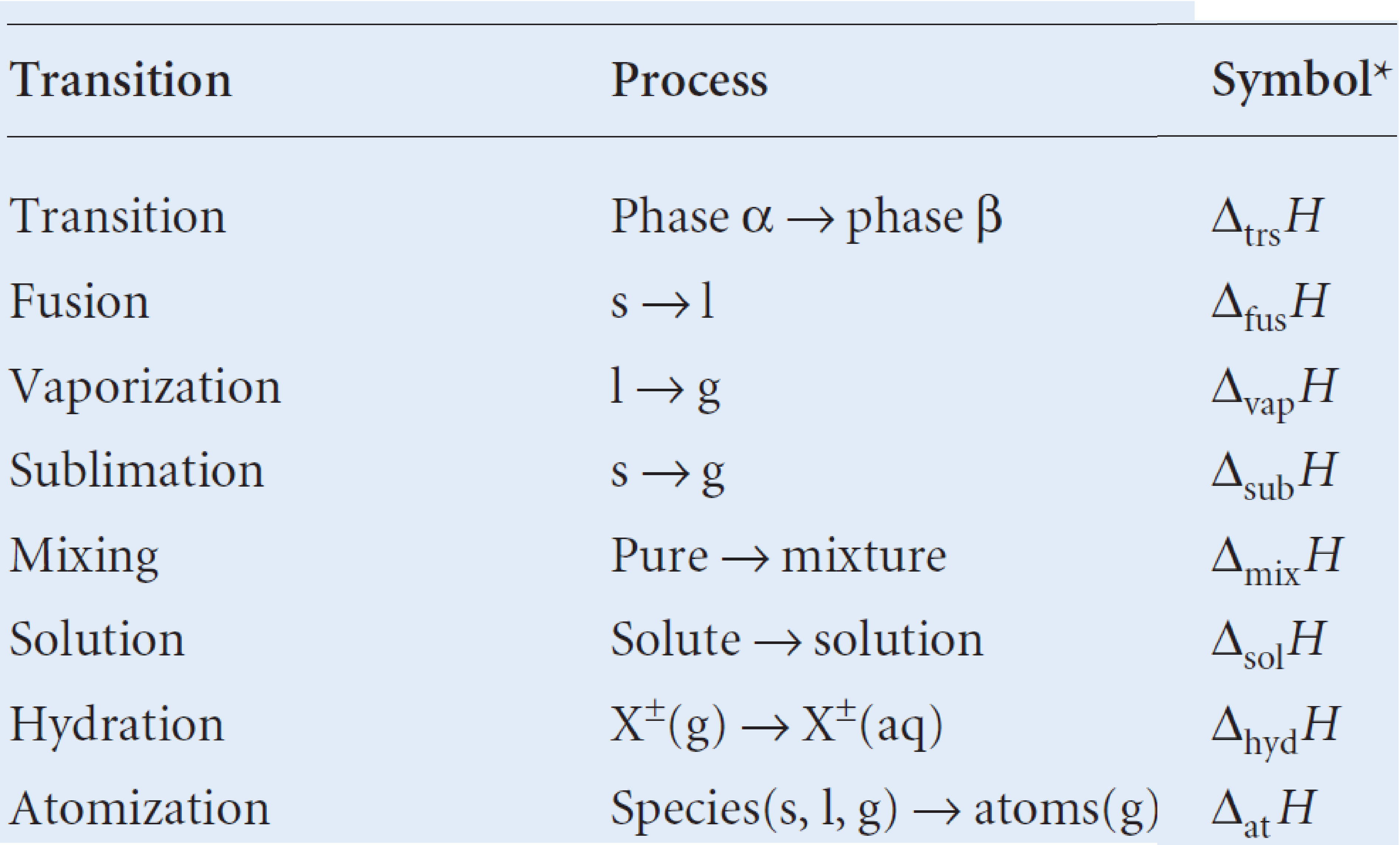
$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta_{fus}H^{\ominus}(273\ \mathrm{K}) = +6.01\ \mathrm{kJ\ mol^{-1}}$$

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta_{vap}H^{\ominus}(373\ \mathrm{K}) = +40.66\ \mathrm{kJ\ mol^{-1}}$$

$$H_2O(s) \rightarrow H_2O(g) \qquad \Delta_{sub}H^{\ominus}$$

Ref. Atkins Physical Chemistry 9th edn

Enthalpies of physical change



Transition	Process	Symbol*
Transition	Phase α → phase β	$\Delta_{\mathrm{trs}}H$
Fusion	s → l	$\Delta_{\mathrm{fus}}H$
Vaporization	l → g	$\Delta_{\mathrm{vap}}H$
Sublimation	s → g	$\Delta_{\mathrm{sub}}H$
Mixing	Pure → mixture	$\Delta_{\mathrm{mix}}H$
Solution	Solute → solution	$\Delta_{\mathrm{sol}}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{\mathrm{hyd}}H$
Atomization	Species(s, l, g) → atoms(g)	$\Delta_{\mathrm{at}}H$

Enthalpies of physical change

Transition	Process	Symbol*
Ionization	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_{ion}H$
Electron gain	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{eg}H$
Reaction	Reactants → products	$\Delta_r H$
Combustion	$\text{Compound}(s, l, g) + O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_c H$
Elements → compound		$\Delta_f H$
Reactants → activated complex		$\Delta^{\ddagger}H$

Enthalpies of physical change

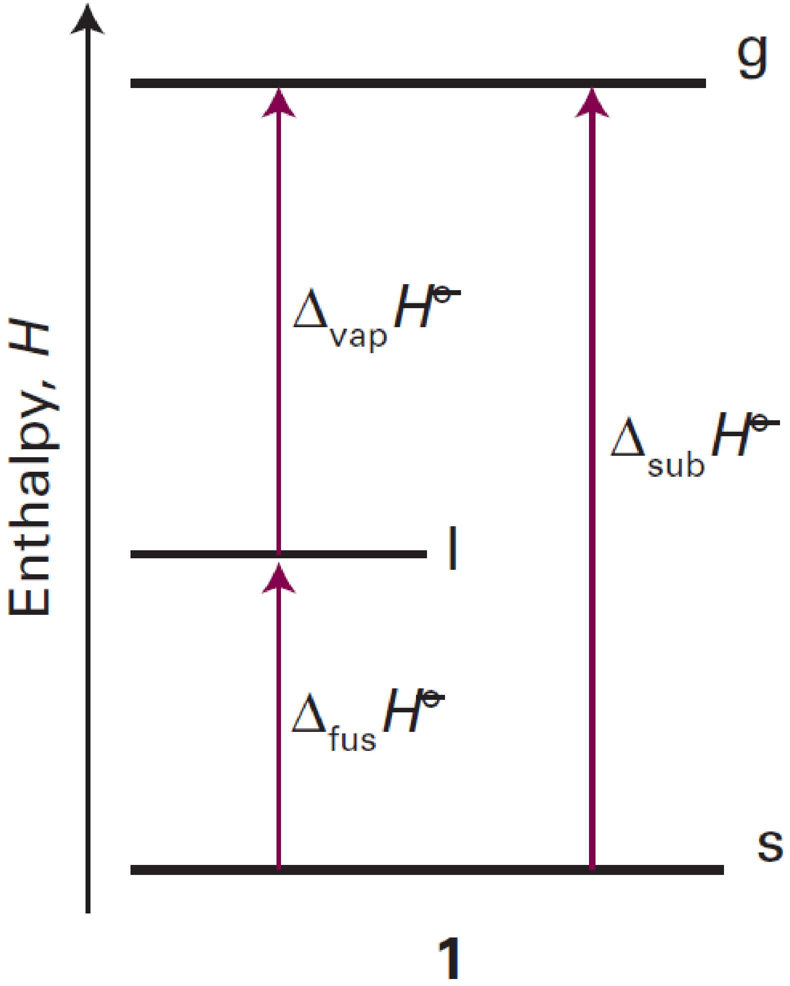
$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta_{fus}H^{\ominus}$$

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta_{vap}H^{\ominus}$$

$$\text{Overall: } H_2O(s) \rightarrow H_2O(g) \qquad \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}$$

$$\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}$$

Enthalpies of physical change



Enthalpies of chemical change

There are two ways of reporting the change in enthalpy that accompanies a chemical reaction.

- One is to write the **thermochemical equation**, a combination of a chemical equation and the corresponding change in standard enthalpy:

$$\mathrm{CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)} \qquad \Delta H^{\ominus} = -890\ \mathrm{kJ}$$

at 298.15 K

$\Delta H^{\ominus}$ is the change in enthalpy when reactants in their standard states change to products in their standard states:

Pure, separate reactants in their standard states

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

For the combustion of methane, the standard value refers to the reaction in which 1 mol CH_4 in the form of pure methane gas at 1 bar reacts completely with 2 mol O_2 in the form of pure oxygen gas at 1 bar to produce 1 mol CO_2 as pure
carbon dioxide gas at 1 bar and 2 mol H_2O as pure liquid water at 1 bar; the numerical
value is for the reaction at 298.15 K.

- Alternatively, we write the chemical equation and then report the **standard reaction enthalpy**, $\Delta_r H^\ominus$

Thus, for the combustion of methane, we write

$$\mathrm{CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)} \qquad \boxed{\Delta_r H^\ominus = -890\ \mathrm{kJ\ mol^{-1}}}$$

For a reaction of the form 2 A + B → 3 C + D the standard reaction enthalpy would be

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

In this case 'per mole' in $\Delta_r H^\ominus$ means 'per 2 mol A', 'per mole B', 'per 3 mol C', or 'per mol D'.

In general,

$$\Delta_{\mathrm{r}} H^{\ominus} = \sum_{\text{Products}} \nu H^{\ominus}_{\mathrm{m}} - \sum_{\text{Reactants}} \nu H^{\ominus}_{\mathrm{m}}$$

Definition of standard reaction enthalpy

Some standard reaction enthalpies have special names and a particular significance. For instance, the **standard enthalpy of combustion**,

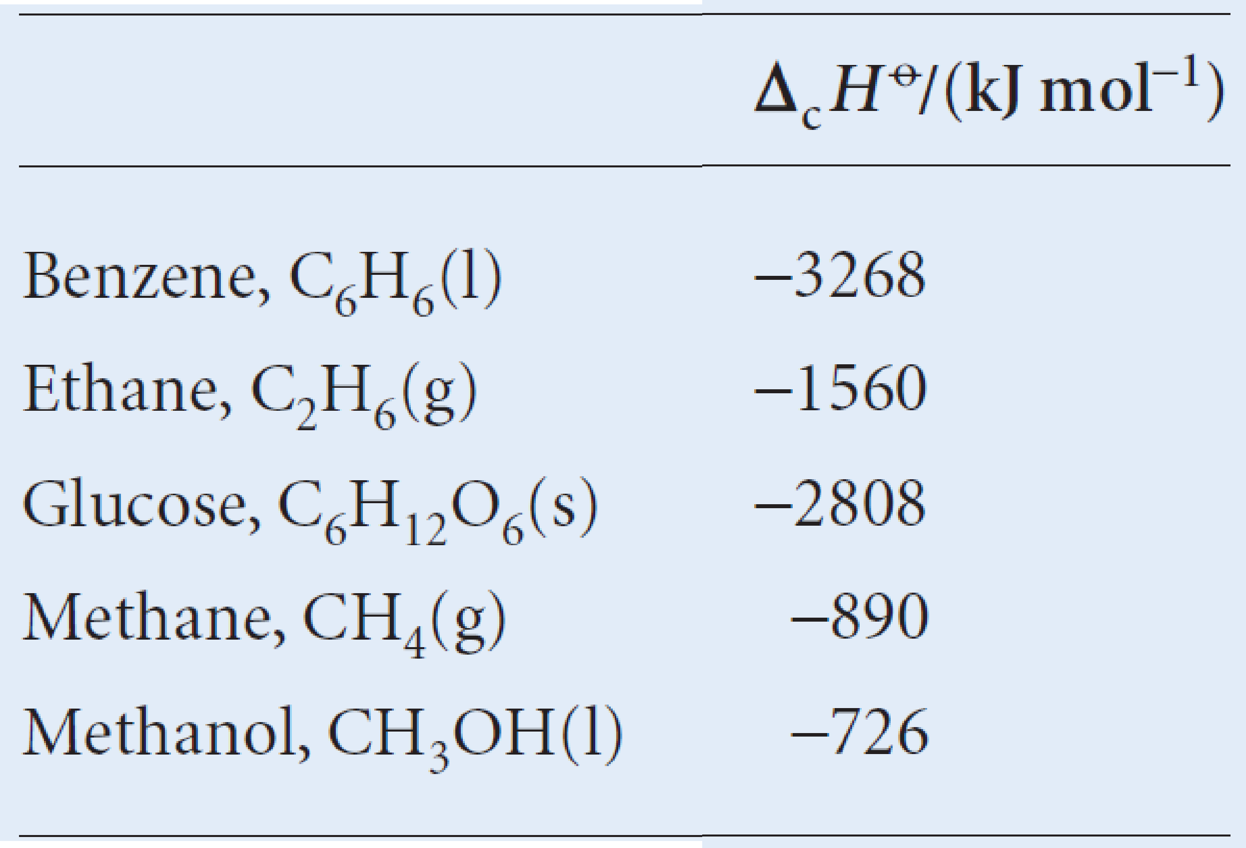
$$\Delta_c H^{\ominus}$$

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(l)$$

$$\Delta_c H^{\ominus} = -2808\ \text{kJ mol}^{-1}$$

The value quoted shows that 2808 kJ of heat is released when 1 mol $C_6H_{12}O_6$ burns under standard conditions (at 298 K).

Standard enthalpies of combustion of organic compounds at 298 K



	$\Delta_c H^\ominus/(\mathrm{kJ\ mol^{-1}})$
Benzene, $C_6H_6(l)$	–3268
Ethane, $C_2H_6(g)$	–1560
Glucose, $C_6H_{12}O_6(s)$	–2808
Methane, $CH_4(g)$	–890
Methanol, $CH_3OH(l)$	–726

Lecture-3

Contents

- Laws of thermochemistry
- Applications of the laws of thermochemistry

Laws of thermochemistry

1. Lavoisier and Laplace’s law

The heat change accompanying a chemical reaction in one direction is exactly equal in magnitude but opposite in sign to that associated with the same reaction in the reverse direction.

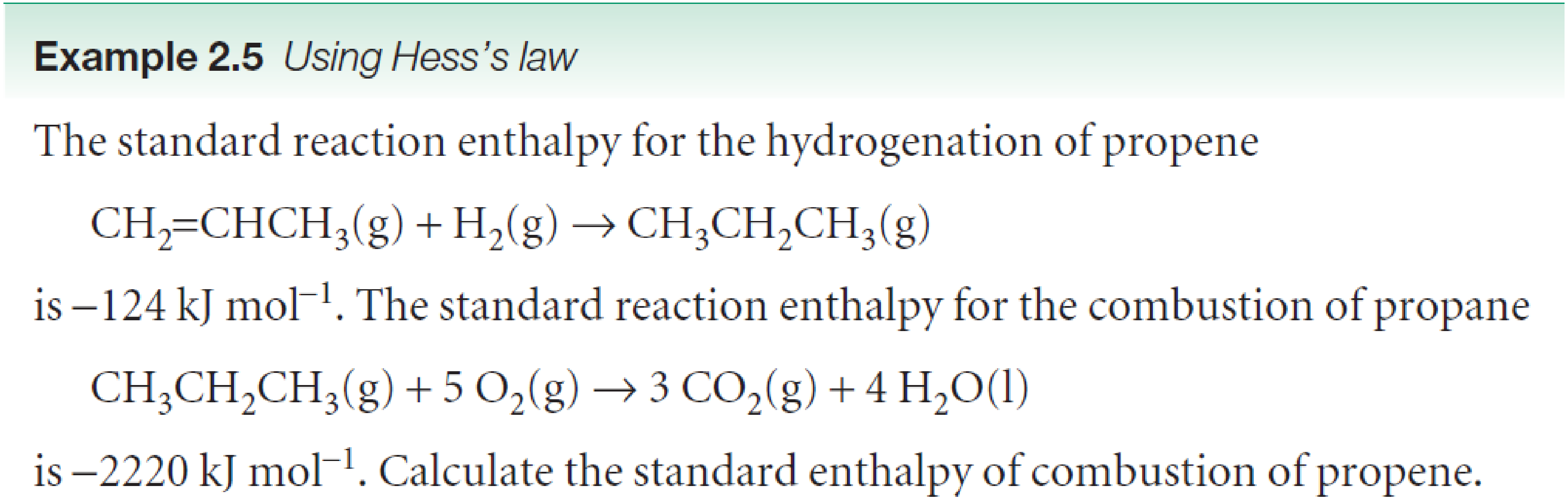
$$CH_4(g) + O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -890.3 \text{ kJ mol}^{-1}$$

$$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + O_2(g) \qquad \Delta H^\circ = +890.3 \text{ kJ mol}^{-1}$$

2. Hess’s law

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.



Example 2.5 *Using Hess’s law*

The standard reaction enthalpy for the hydrogenation of propene

$$CH_2{=}CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$$

is -124 kJ mol^{-1}. The standard reaction enthalpy for the combustion of propane

$$CH_3CH_2CH_3(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

is -2220 kJ mol^{-1}. Calculate the standard enthalpy of combustion of propene.

Method

The skill to develop is the ability to assemble a given thermochemical equation from others. Add or subtract the reactions given, together with any others needed, so as to reproduce the reaction required. Then add or subtract the reaction enthalpies in the same way.

Answer The combustion reaction we require is

$$C_3H_6(g) + \tfrac{9}{2}\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$$

This reaction can be recreated from the following sum:

$$\begin{array}{lr}
 & \Delta_r H^{\ominus}/(\mathrm{kJ\ mol^{-1}}) \\
C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g) & -124 \\
C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l) & -2220 \\
H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}\,O_2(g) & +286 \\
\hline
C_3H_6(g) + \tfrac{9}{2}\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l) & -2058
\end{array}$$

Exercises

1. From the following data, determine $\Delta_f H^0$ for diborane, B_2H_6(g), at 298 K:

$$(1)\quad B_2H_6(g) + 3\,O_2(g) \rightarrow B_2O_3(s) + 3\,H_2O(g) \qquad \Delta_r H^\ominus = -2036\ \text{kJ mol}^{-1}$$

$$(2)\quad 2\,B(s) + \tfrac{3}{2}\,O_2(g) \rightarrow B_2O_3(s) \qquad \Delta_r H^\ominus = -1274\ \text{kJ mol}^{-1}$$

$$(3)\quad H_2(g) + \tfrac{1}{2}\,O_2(g) \rightarrow H_2O(g) \qquad \Delta_r H^\ominus = -241.8\ \text{kJ mol}^{-1}$$

2. Calculate the enthalpy of hydrogenation of benzene from its enthalpy of combustion and the enthalpy of combustion of cyclohexane. [–205 kJ mol^{-1}]

Ref. Atkins Physical Chemistry 9th edn

Applications of laws of thermochemistry

- Determination of heat of formation of substances which otherwise cannot be measured experimentally
- Determination of heat of transition
- Determination of heats of various reactions

Determination of heat of formation of substances which otherwise cannot be measured experimentally

$$K(s) + H_2O\,(aq) \longrightarrow KOH + \tfrac{1}{2}H_2 \qquad \Delta H = -48.0\,\text{kcal} \qquad (i)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -68.5\,\text{kcal} \qquad (ii)$$

$$KOH(s) \longrightarrow KOH(aq) \qquad \Delta H = -14.0\,\text{kcal} \qquad (iii)$$

Adding equations (*i*) and (*ii*) and subtracting equation (*iii*) will give

$$K(s) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow KOH(s) \qquad \Delta H = -102.5\,\text{kcal}$$

Thus heat of formation of KOH is – **102.5 kcal**.

Determination of heat of transition

Example

$$S_{\text{rhombic}} + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -291.4\,\text{kJ} \quad \text{----(1)}$$

$$S_{\text{monoclinic}} + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H = -295.4\,\text{kJ} \quad \text{----(2)}$$

Subtracting equation (2) from (1) we get

$$S_{\text{rhombic}} = S_{\text{monoclinic}} \qquad \Delta H = 4.0\,\text{kJ}$$

Thus heat of transition of rhombic sulphur to monoclinic sulphur is **4.0 kJ.**

Determination of heats of various reactions

Example

From the following equations the enthalpy of dimerization of NO_2 can be calculated.

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = 67.9\,\text{kJ} \qquad \text{----(1)}$$

$$N_2(g) + 2O_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = 9.3\,\text{kJ} \qquad \text{----(2)}$$

Subtracting equation (1) from equation (2) we have

$$2NO_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = (9.3 - 67.9)\,\text{kJ}$$

$$= -58.6\,\text{kJ}$$

Thus the heat of dimerization of NO_2 is – **58.6 kJ.**

Lecture-4

Contents

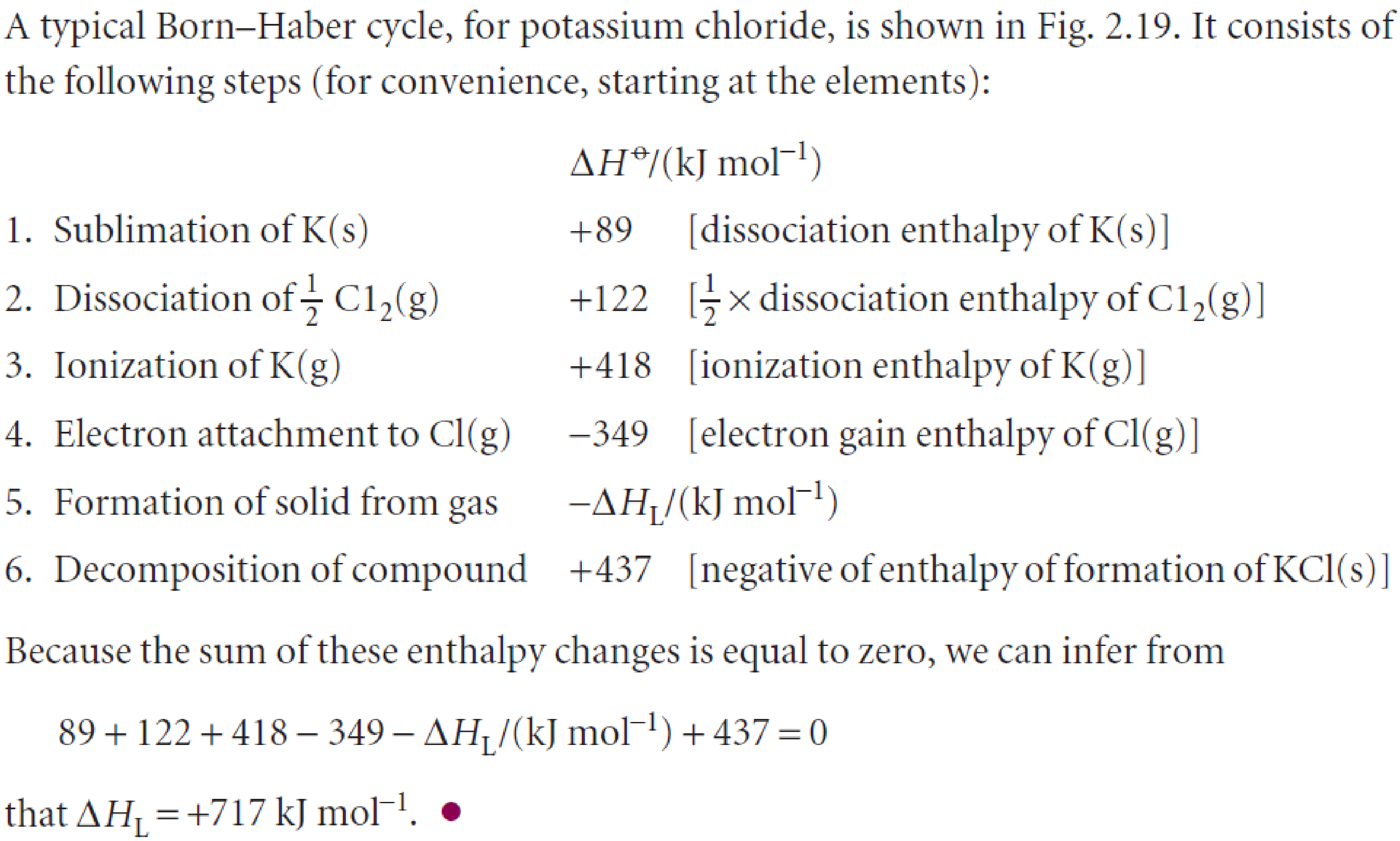
- Born-Haber cycle
- Bond enthalpy
- Calorific value of foods and fuels

Born–Haber cycle

- The **Born–Haber cycle** is an approach to analyze reaction energies.
- Born–Haber cycles are used primarily as a means of calculating lattice energy, which cannot otherwise be measured directly.
- It applies Hess's law to calculate the lattice enthalpy by comparing the standard enthalpy change of formation of the ionic compound (from the elements) to the enthalpy required to make gaseous ions from the elements.

Born–Haber cycle

- **A brief illustration**



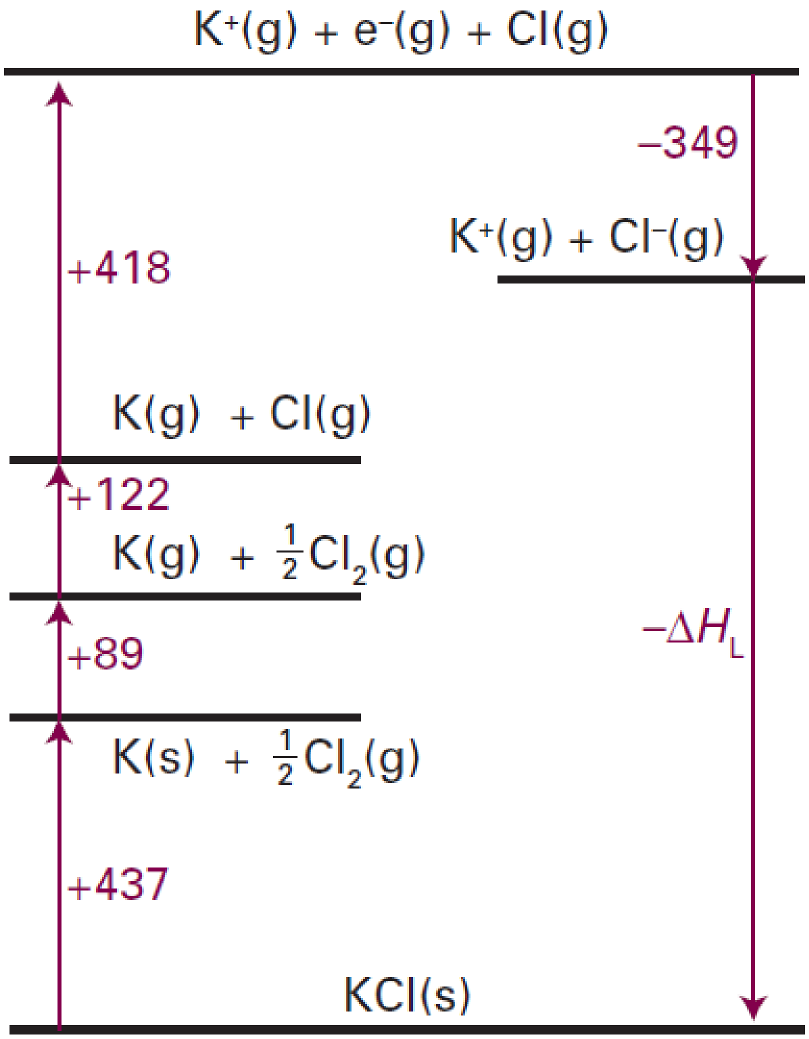
A typical Born–Haber cycle, for potassium chloride, is shown in Fig. 2.19. It consists of the following steps (for convenience, starting at the elements):

	$\Delta H^\ominus/(\mathrm{kJ\ mol^{-1}})$	
1. Sublimation of K(s)	+89	[dissociation enthalpy of K(s)]
2. Dissociation of $\frac{1}{2}\,\mathrm{C1_2(g)}$	+122	[$\frac{1}{2}\times$ dissociation enthalpy of $\mathrm{C1_2(g)}$]
3. Ionization of K(g)	+418	[ionization enthalpy of K(g)]
4. Electron attachment to Cl(g)	−349	[electron gain enthalpy of Cl(g)]
5. Formation of solid from gas	$-\Delta H_L/(\mathrm{kJ\ mol^{-1}})$	
6. Decomposition of compound	+437	[negative of enthalpy of formation of KCl(s)]

Because the sum of these enthalpy changes is equal to zero, we can infer from

$$89 + 122 + 418 - 349 - \Delta H_L/(\mathrm{kJ\ mol^{-1}}) + 437 = 0$$

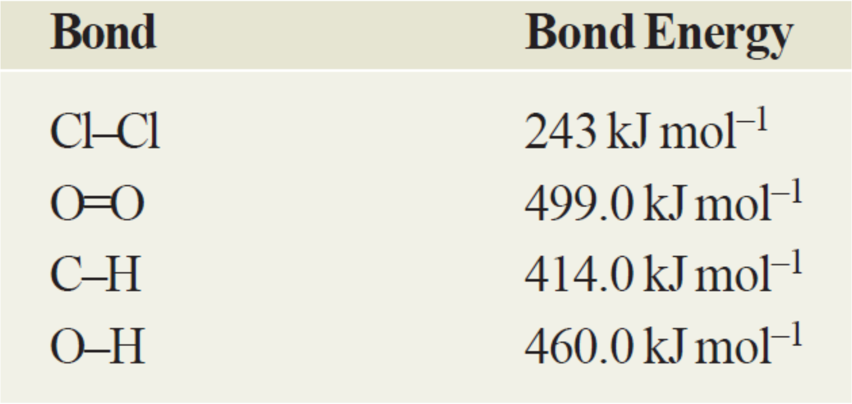
that $\Delta H_L = +717\ \mathrm{kJ\ mol^{-1}}$. ●



The Born–Haber cycle for KCl at 298 K. Enthalpies changes are in kilojoules per mole.

Bond enthalpy/energy

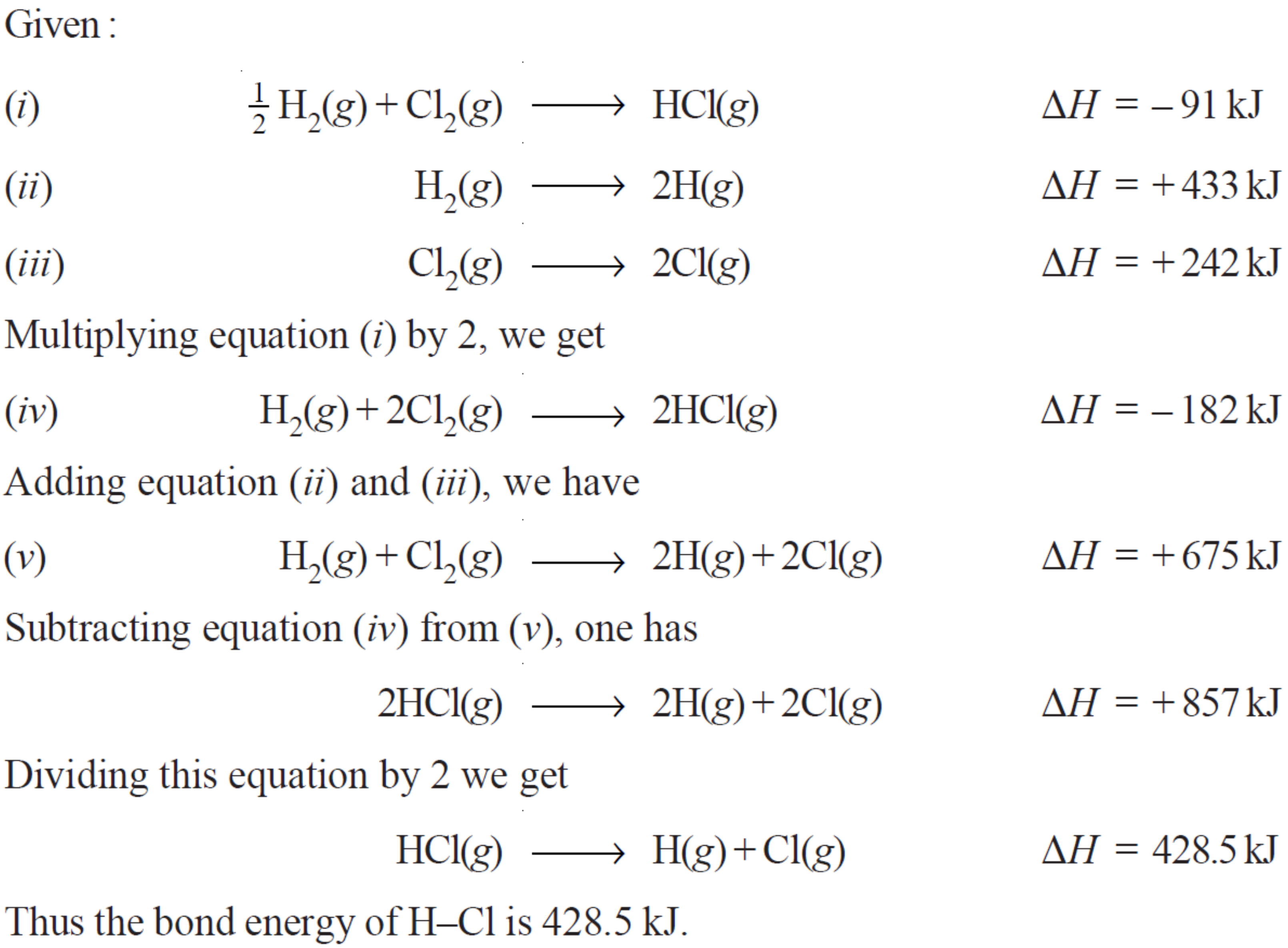
Bond enthalpy/energy is defined as the energy necessary to break one mole of bonds between two atoms in a gaseous substance to form gaseous atoms or species.



Bond	Bond Energy
Cl–Cl	243 kJ mol^{-1}
O=O	499.0 kJ mol^{-1}
C–H	414.0 kJ mol^{-1}
O–H	460.0 kJ mol^{-1}

Bond energy is a measure of strength of the bond.

Calculate the bond energy of HCl, given that H–H bond energy is 433 kJ mol^{-1}, Cl – Cl bond energy is 242 kJ mol^{-1} and ΔH_f for HCl is – 91 kJ mol^{-1}.



Given :

$$(i) \quad \tfrac{1}{2}H_2(g) + Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H = -91\,\text{kJ}$$

$$(ii) \quad H_2(g) \longrightarrow 2H(g) \qquad \Delta H = +433\,\text{kJ}$$

$$(iii) \quad Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H = +242\,\text{kJ}$$

Multiplying equation (*i*) by 2, we get

$$(iv) \quad H_2(g) + 2Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -182\,\text{kJ}$$

Adding equation (*ii*) and (*iii*), we have

$$(v) \quad H_2(g) + Cl_2(g) \longrightarrow 2H(g) + 2Cl(g) \qquad \Delta H = +675\,\text{kJ}$$

Subtracting equation (*iv*) from (*v*), one has

$$2HCl(g) \longrightarrow 2H(g) + 2Cl(g) \qquad \Delta H = +857\,\text{kJ}$$

Dividing this equation by 2 we get

$$HCl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H = 428.5\,\text{kJ}$$

Thus the bond energy of H–Cl is 428.5 kJ.

Calorific value of foods and fuels

The calorific value is defined as the amount of heat produced when one gram of a substance is completely burnt.

$$\mathrm{CH_4}(g) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\mathrm{H_2O}(l) \qquad \Delta H_c = -890.3\ \mathrm{kJ}$$

$$\mathrm{C_2H_6}(g) + 3\tfrac{1}{2}\,\mathrm{O_2}(g) \longrightarrow 2\mathrm{CO_2}(g) + 3\mathrm{H_2O}(l) \qquad \Delta H_c = -1559.7\ \mathrm{kJ}$$

In case of methane heat produced per gram is 890.3/16 = 55.64 kJ g^{-1} while for ethane it is 1559.7/30 = 51.90 kJ g^{-1}. Thus methane has better fuel efficiency than ethane as it produces more heat per gram.

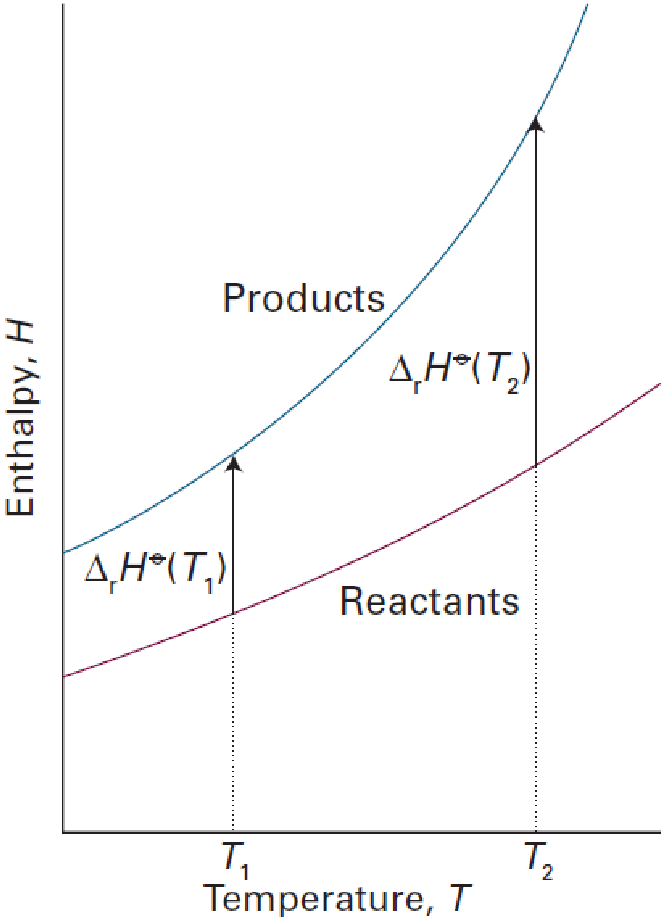
Lecture-5

Contents

- Temperature dependence of reaction enthalpies: Kirchhoff’s law
- Mathematical problems related to Kirchhoff’s law

The temperature dependence of reaction enthalpies : Kirchhoff’s law

- When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents.
- In each case, the change in enthalpy depends on the heat capacities of the substances.
- The change in reaction enthalpy reflects the difference in the changes of the enthalpies.



An illustration of the content of Kirchhoff’s law.

Kirchhoff's law

At constant pressure

$$\mathrm{d}H = C_p \mathrm{d}T \quad \text{(at constant pressure)}$$

When a substance is heated from T_1 to T_2, its enthalpy changes from $H(T_1)$ to

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \mathrm{d}T$$

Because this equation applies to each substance in the reaction, the standard reaction enthalpy changes from $\Delta_r H^\ominus(T_1)$ to

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

Kirchhoff's law

where $\Delta_r C_p^\ominus$ s the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in
the chemical equation:

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

Example 2.6 *Using Kirchhoff's law*

The standard enthalpy of formation of $H_2O(g)$ at 298 K is -241.82 kJ mol^{-1}. Estimate its value at 100°C given the following values of the molar heat capacities at constant pressure: $H_2O(g)$: 33.58 J K^{-1} mol^{-1}; $H_2(g)$: 28.82 J K^{-1} mol^{-1}; $O_2(g)$: 29.36 J K^{-1} mol^{-1}. Assume that the heat capacities are independent of temperature.

Ref. Physical Chemistry, Atkins and Paula, 9th edn.

Method

When $\Delta C_p^{\ominus}$s independent of temperature in the range T_1 to T_2, the integral evaluates to $(T_2 - T_1)$. T$\Delta_r C_p^{\ominus}$ore,

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

To proceed,

- write the chemical equation,
- identify the stoichiometric coefficients,
- and calculate $\Delta_r C_p^{\ominus}$ from the data.

Answer

The reaction is

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g), \text{ so}$$

$$\Delta_r C_p^{\ominus} = C_{p,m}^{\ominus}(H_2O,g) - \{C_{p,m}^{\ominus}(H_2,g) + \tfrac{1}{2}C_{p,m}^{\ominus}(O_2,g)\}$$

$$= -9.92\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

It then follows that

$$\Delta_r H^{\ominus}(373\ \mathrm{K}) = -241.82\ \mathrm{kJ\ mol^{-1}} + (75\ \mathrm{K}) \times (-9.92\ \mathrm{J\ K^{-1}\ mol^{-1}})$$

$$= -242.6\ \mathrm{kJ\ mol^{-1}}$$

Self-test 2.7

Estimate the standard enthalpy of formation of cyclohexane, $C_6H_{12}(l)$, at 400 K. [$-163\ \mathrm{kJ\ mol^{-1}}$]

Standard enthalpy of formation of $C_6H_{12}(l)$ at 298 K is -156 kJ $\mathrm{mol^{-1}}$. Molar heat capacities of C_6H_{12}, C and H_2 are 156.5 J $\mathrm{K^{-1}\ mol^{-1}}$, 8.66 J $\mathrm{K^{-1}\ mol^{-1}}$, 28.8 J $\mathrm{K^{-1}\ mol^{-1}}$, respectively.

Lecture-6

Contents

- Calorimetry
- Constant pressure calorimeter
- Adiabatic flame calorimeter
- Bomb calorimeter
- Differential scanning calorimeter
- Home work: Definition of enthalpies of some processes

Calorimetry

- **Calorimetry** is the study of the transfer of energy as heat during a physical or chemical process.
- A **calorimeter** is a device for measuring energy transferred as heat.

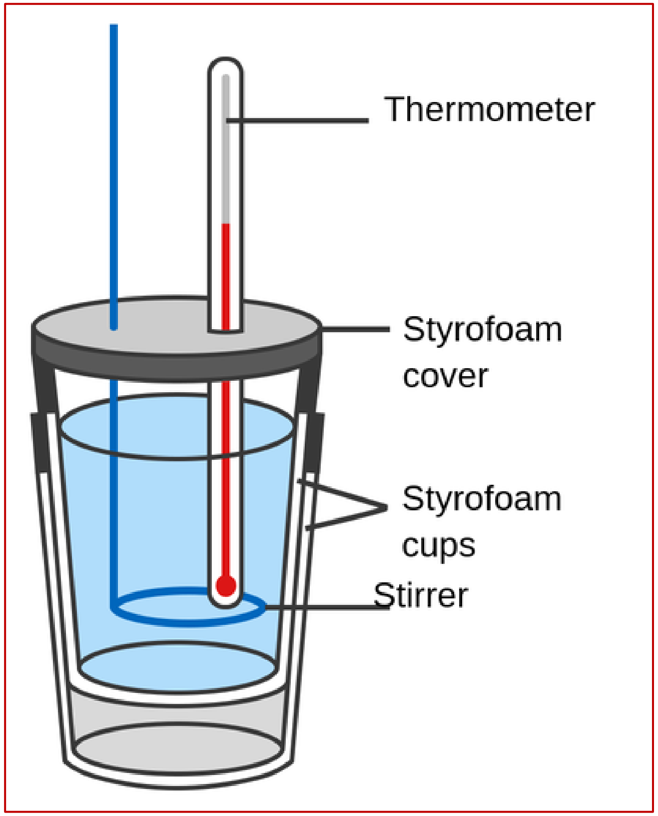
The most common devices used in calorimetry

- Constant pressure calorimeter
- Adiabatic flame calorimeter
- Bomb calorimeter
- Differential scanning calorimeter (DSC)

Constant pressure calorimeter

The energy released as heat in the reaction is monitored by measuring the change in temperature of the contents.

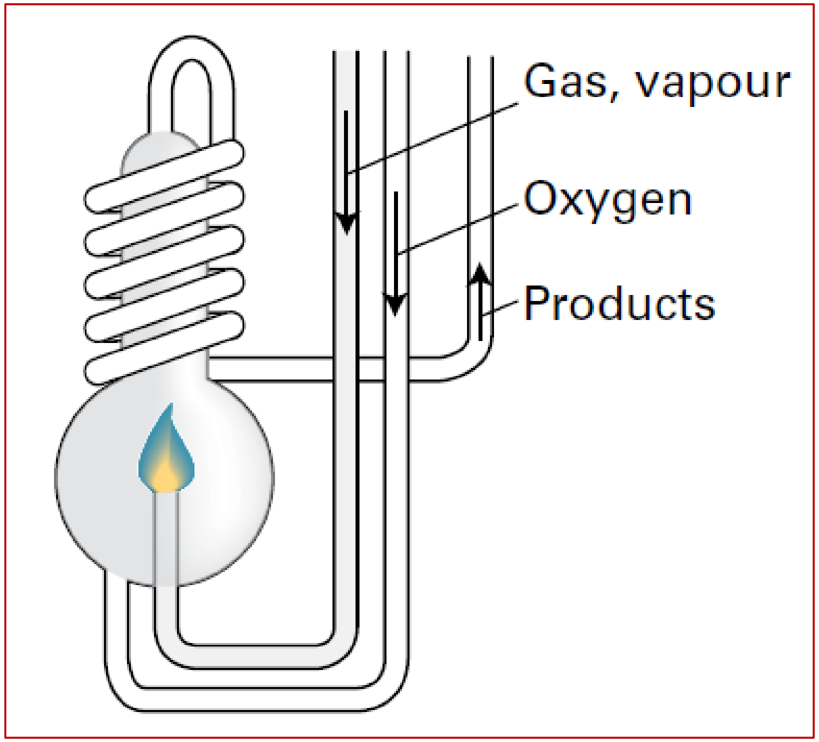
A constant-pressure calorimeter measures the change in enthalpy of a reaction occurring in a liquid solution. The heat transferred to/from the solution in order for the reaction to occur is equal to the change in enthalpy ($\Delta H = q_P$).



$$q_P = C_{P,s} \times m \times \Delta T$$

Adiabatic flame calorimeter

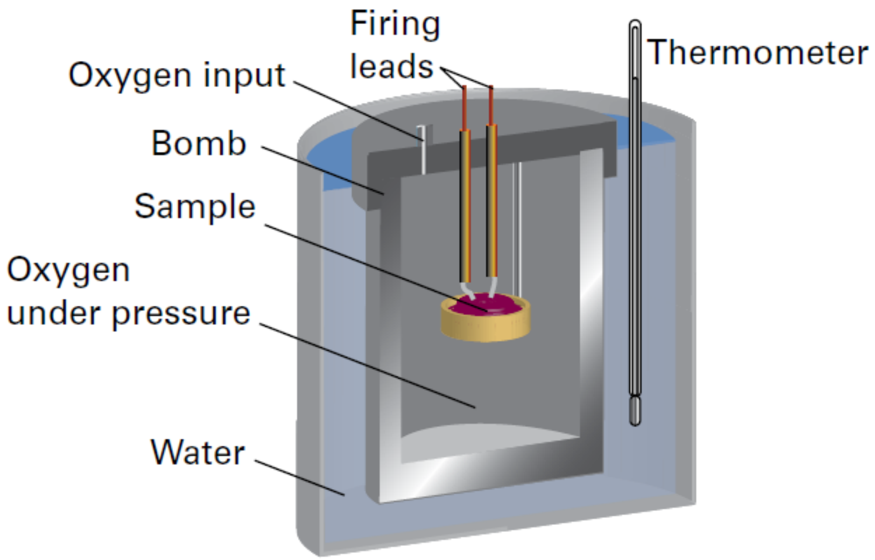
- For a combustion reaction an adiabatic flame calorimeter may be used.
- To measure Δ*T,* a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.



A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath.

Bomb calorimeter

Change in internal energy, ΔU is measured by using a bomb calorimeter and then ΔU is converted to ΔH.



A constant-volume bomb calorimeter. The ‘bomb’ is the central vessel, which is strong enough to withstand high pressures. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

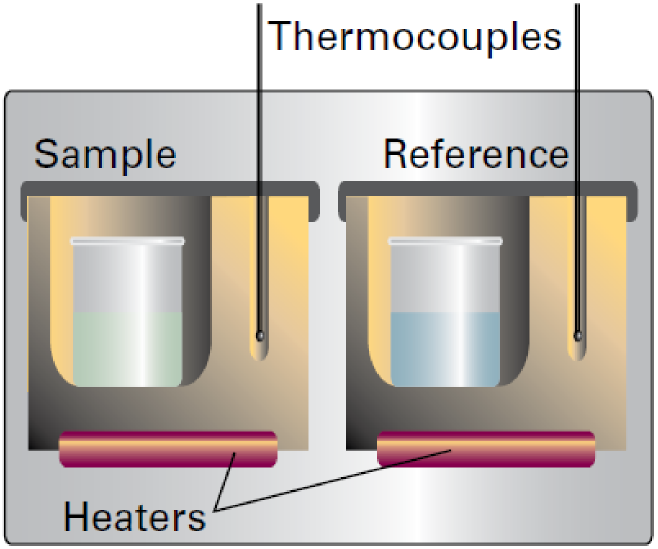
Differential Scanning Calorimetry

- **A differential scanning calorimeter** (DSC) measures the energy transferred as heat to or from a sample at constant pressure during a physical or chemical change.
- The term ‘differential’ refers to the fact that measurements on a sample are compared to those on a reference material that does not undergo a physical or chemical change during the analysis.
- The term ‘scanning’ refers to the fact that the temperatures of the sample and reference material are increased, or scanned, during the analysis.

Differential Scanning Calorimeter (DSC)

DSC measures the energy transferred as heat to or from a sample at constant pressure during a physical or chemical change.

- A DSC consists of two small compartments that are heated electrically at a constant rate.



DSC

- The sample and a reference material are heated in separate but identical metal heat sinks.
- The output is the difference in power needed to maintain the heat sinks at equal temperatures as the temperature rises.

Differential Scanning Calorimeter (DSC)

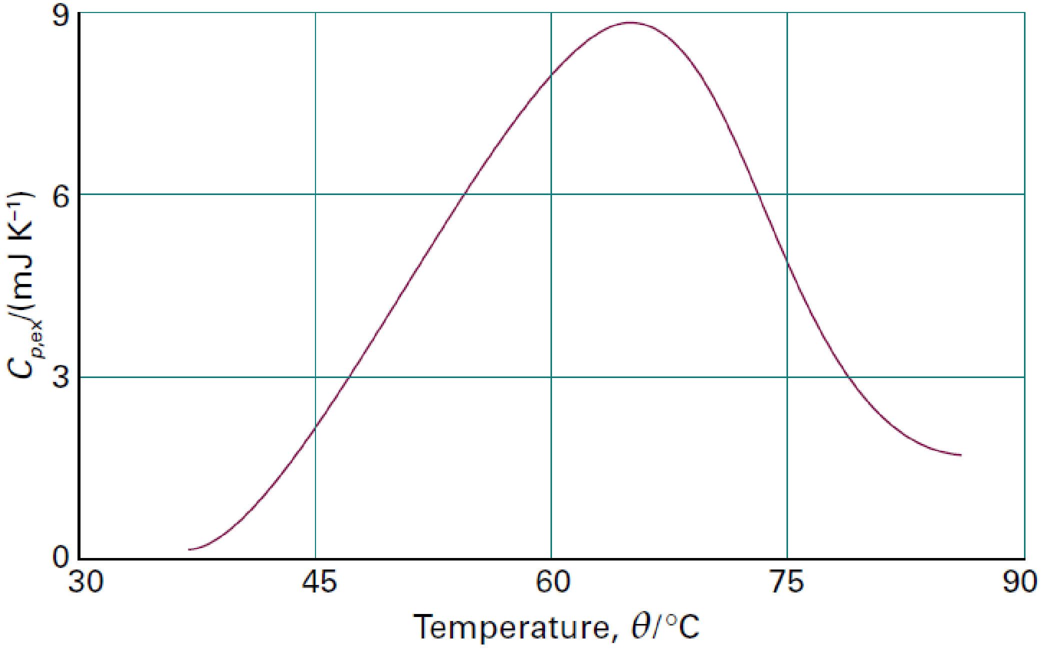
- The temperature, T, at time t during a linear scan is $T = T_0 + \alpha t$, where T_0 is the initial temperature and α is the scan rate.
- A computer controls the electrical power supply that maintains the same temperature in the sample and reference compartments throughout the analysis.
- If no physical or chemical change occurs in the sample at temperature T, the heat transferred to the sample is written as $q_p = C_p \Delta T$, where $\Delta T = T - T_0$ and C_p is assumed to be independent of temperature. Because $T = T_0 + \alpha t$, it follows that $\Delta T = \alpha t$.

- If a chemical or physical process takes place, the energy required to be transferred as heat to attain the same change in temperature of the sample as the control is $q_p + q_{p,ex}$.
- The quantity $q_{p,\mathrm{ex}}$ is interpreted in terms of an apparent change in the heat capacity at constant pressure, from C_p to $C_p + C_{p,ex}$ of the sample during the temperature scan:

$$\boxed{C_{p,\mathrm{ex}} = \frac{q_{p,\mathrm{ex}}}{\Delta T} = \frac{q_{p,\mathrm{ex}}}{\alpha t} = \frac{P_{\mathrm{ex}}}{\alpha}}$$

where $P_{\mathrm{ex}} = q_{p,\mathrm{ex}}/t$ is the excess electrical power necessary to equalize the temperature of the sample and reference compartments.

A DSC trace, also called a **thermogram**, consists of a plot of $C_{p,\text{ex}}$ against *T.*



A thermogram for the protein ubiquitin at pH = 2.45. The protein retains its native structure up to about 45 °C and then undergoes an endothermic conformational change.

The enthalpy change associated with the process is

$$\Delta H = \int_{T_1}^{T_2} C_{p,\mathrm{ex}}\,\mathrm{d}T$$

where T_1 and T_2 are, respectively, the temperatures at which the process begins and ends. This relation shows that the enthalpy change is equal to the area under the plot of $C_{p,\mathrm{ex}}$ against T.

Home work

Define enthalpy of neutralization, enthalpy of solution, enthalpy of hydration, enthalpy of fusion, enthalpy of vaporization, enthalpy of sublimation and lattice enthalpy.

Lecture-7

Contents

- Class assessment