CHEMICAL THERMODYNAMICS

Part 2

8.3 THE FIRST LAW OF THERMODYNAMICS

Dissolving NaCl in water:

The solution gets colder as the salt dissolves.

Heat is absorbed by the **system** from the **surroundings**.

Dissolving LiCl in water:

The solution becomes hot as the salt dissolves.

Heat is released by the **system** into the **surroundings**.

8.3 THE FIRST LAW OF THERMODYNAMICS

A chemical system can exchange energy with its surroundings in two ways:

heat (*Q*) and **work** (*W*)

The energy that is transferred changes the object's internal energy.

8.3 THE FIRST LAW OF THERMODYNAMICS

The **change** in the internal energy of the system that accompanies a process:

$$\Delta U = U_{\text{final}} - U_{\text{initial}}$$

$$\Delta_r U = U_{\text{products}} - U_{\text{reactants}}$$

8.3 THE FIRST LAW OF THERMODYNAMICS

- **Work** may be defined simply as motion against an opposite force.
- In chemical systems, this is frequently the compression or expansion of gas:
- Pressure-volume or ***p·V*** **work**

$$\Delta W = -p \cdot \Delta V$$

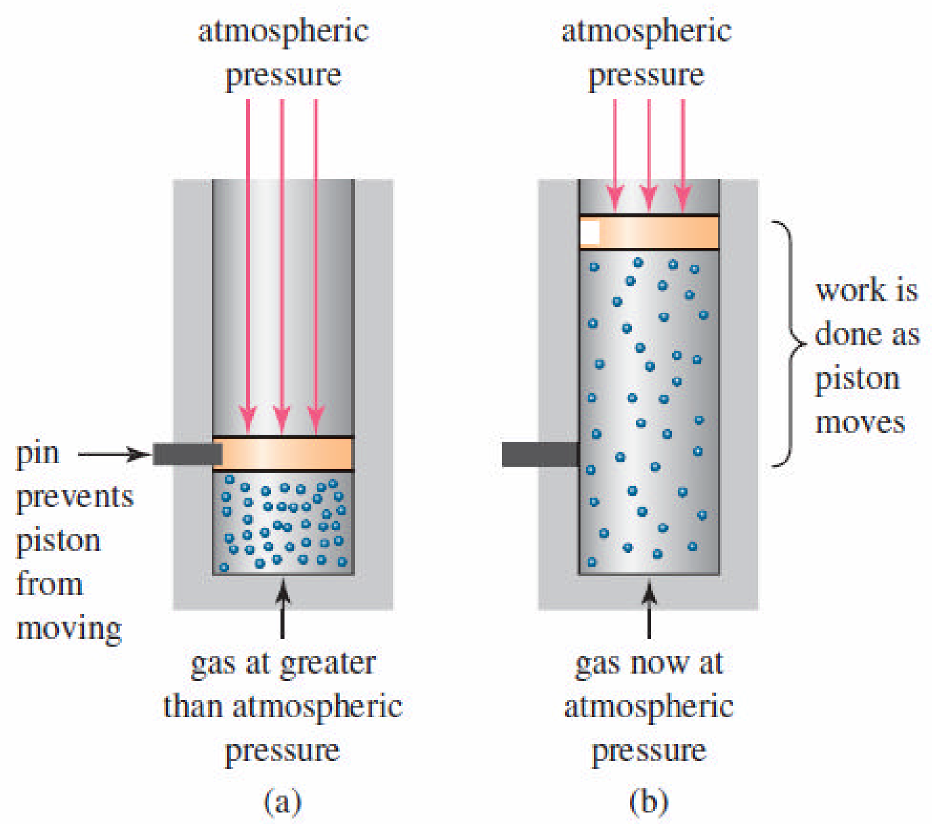


Figure from Blackman *et al.* (2016) *Chemistry*. 3rd Edn., Wiley

8.3 THE FIRST LAW OF THERMODYNAMICS

First law of thermodynamics

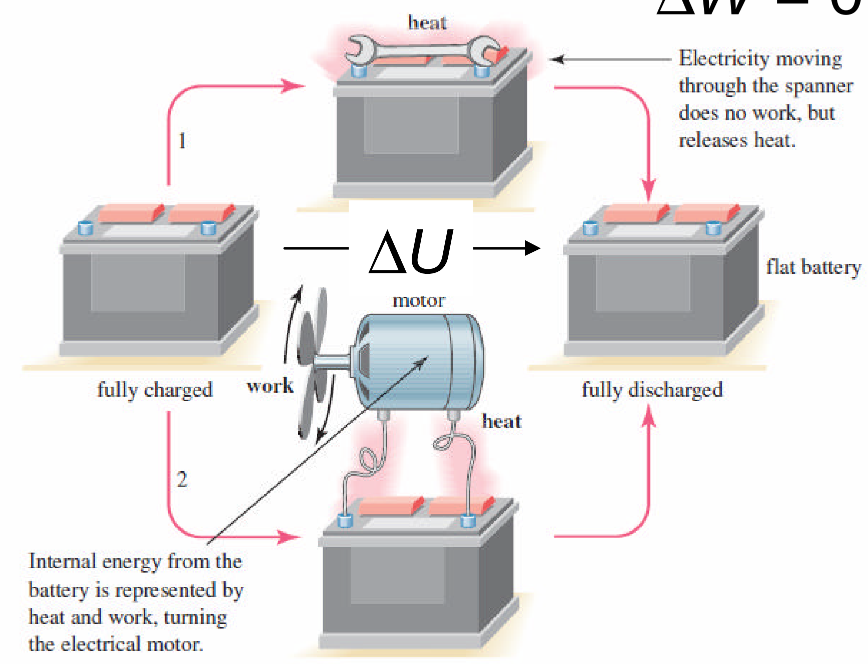
$$\Delta U = \Delta Q + \Delta W$$

- Energy can be transferred between systems as either heat or work
- It can never be created or destroyed
- Law of conservation of energy

8.3 THE FIRST LAW OF THERMODYNAMICS

- *Q* and *W* are **not** state functions.
- The values of *Q* and *W* are dependent on the path of change.

$\Delta Q \neq 0$
$\Delta W = 0$



$\Delta Q \neq 0$
$\Delta W \neq 0$

Figure from Blackman *et al.* (2016) *Chemistry*. 3rd Edn., Wiley

8.3 THE FIRST LAW OF THERMODYNAMICS

Heat capacity

- Heat and temperature are not the same thing
- Heat is a transfer of energy due to a temperature difference

$$\Delta Q = C \cdot \Delta T$$

Q:	heat	$[Q] = 1\ \text{J}$
C:	**heat capacity**	$[C] = 1\ \text{J K}^{-1}$
T:	temperature	$[T] = 1\ \text{K}$

8.3 THE FIRST LAW OF THERMODYNAMICS

Extensive and intensive properties

- Heat capacity depends on the size of the sample.
- A property with a value that depends on the size of the sample is an **extensive property**.
- A property with a value independent of the size of the sample is an **intensive property**.

8.3 THE FIRST LAW OF THERMODYNAMICS

Intensive property: specific heat capacity

– Divide heat capacity (extensive property) by the mass of the sample to form the specific heat capacity (intensive property)

$$c = \frac{C}{m}$$

c **specific heat capacity** $[c] = 1\ \mathrm{J\ g^{-1}\ K^{-1}}$

$$\Delta Q = c \cdot m \cdot \Delta T$$

8.3 THE FIRST LAW OF THERMODYNAMICS

Intensive property: molar heat capacity

– Divide heat capacity (extensive property) by the molar amount of the sample to form the molar heat capacity (intensive property)

$$c = \frac{C}{n}$$

c **molar heat capacity** $[c] = 1\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$$\Delta Q = c \cdot n \cdot \Delta T$$

The determination of heat

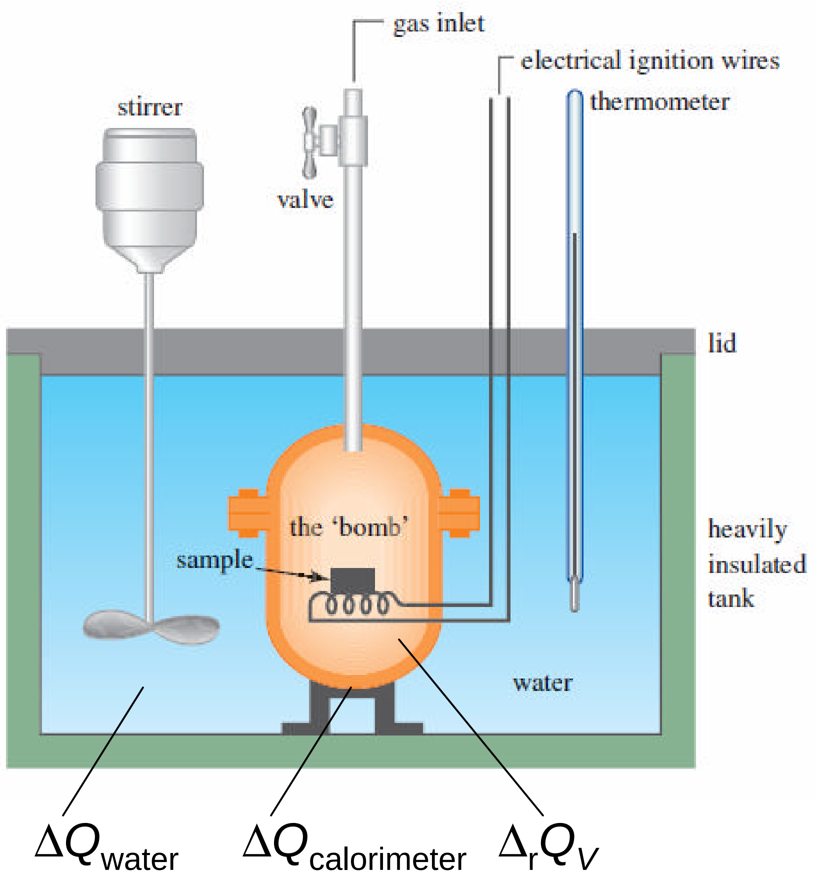
Calorimeter: designed to minimise heat loss between the system and the surroundings.

Bomb calorimeter
System remains at constant volume
V = const. => $\Delta V = 0$ => $p \cdot \Delta V = 0$
i.e. there is no work done

$\Delta U = \Delta Q + \Delta W$
$\Delta_r U = \Delta_r Q_V$

$\Delta_r Q_V$ is the heat of reaction at constant volume.

$\Delta Q_{calorimeter} + \Delta Q_{water} = -\Delta_r Q_V$



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Example

When 1.000 g of olive oil was completely burned in pure oxygen in a bomb calorimeter, the temperature of the surrounding water bath, which contained 0.750 kg of water (c_V = 4.18 J g^{-1} K^{-1}), increased from 22.000°C to 22.241°C. The heat capacity of the bomb calorimeter was 5.896 kJ K^{-1}. How much heat is produced on burning 1.000 g of olive oil?

SUMMARY

- Heat, ΔQ, is transferred from an object at high temperature to one at lower temperature and can be determined by measuring temperature change:

  $$\Delta Q = C \cdot \Delta T$$

- Specific and molar heat capacities are intensive properties of particular substances.
- Pressure-volume work is defined as:

  $$\Delta W = -p \cdot \Delta V$$

SUMMARY

- The first law of thermodynamics states that: $\Delta U = \Delta Q + \Delta W$

- $\Delta U = \Delta Q_v$ can be determined using a bomb calorimeter.

jPoll Question

If the same amount of heat is applied to 1 kg iron and 1 kg water, which are initially at the same temperature, for the same amount of time, what is the result? Data: c(iron) = 0.450 J g^{-1} K^{-1}; c(water) = 4.18 J g^{-1} K^{-1}.

1 The iron sample has a higher temperature than the water sample.
2 The water sample has a higher temperature than the iron sample.
3 Both samples have the same temperature.

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