THERMODYNAMICS

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Why study thermodynamics?

1. All chemical reactions result in heat transfer

2. Understanding heat transfer properties is important for building materials

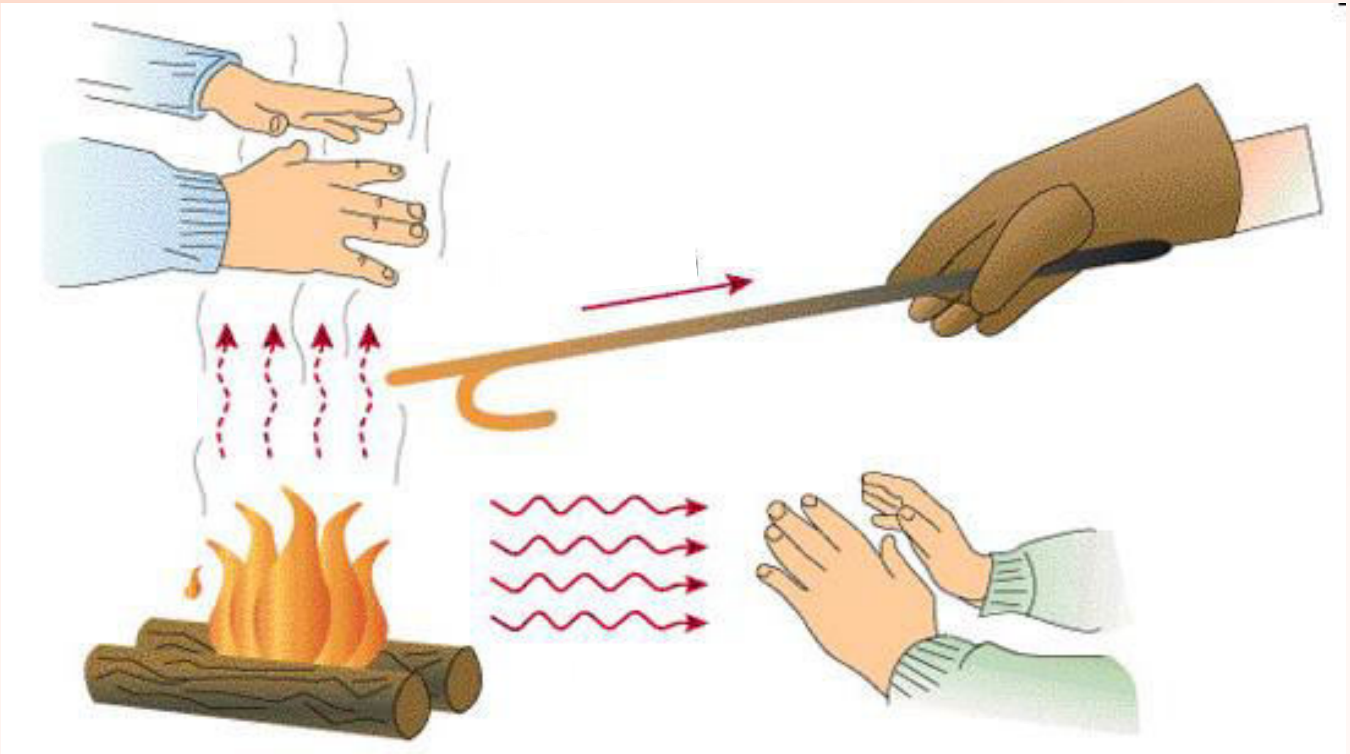
3. Food is evaluated by the amount of energy it releases

HEAT & TEMPERATURE

Heat – the transfer of energy due to contact

Thermal energy – the energy of an object directly related to temperature

Temperature – measure of internal energy of an object due to particle motion (kinetic energy)

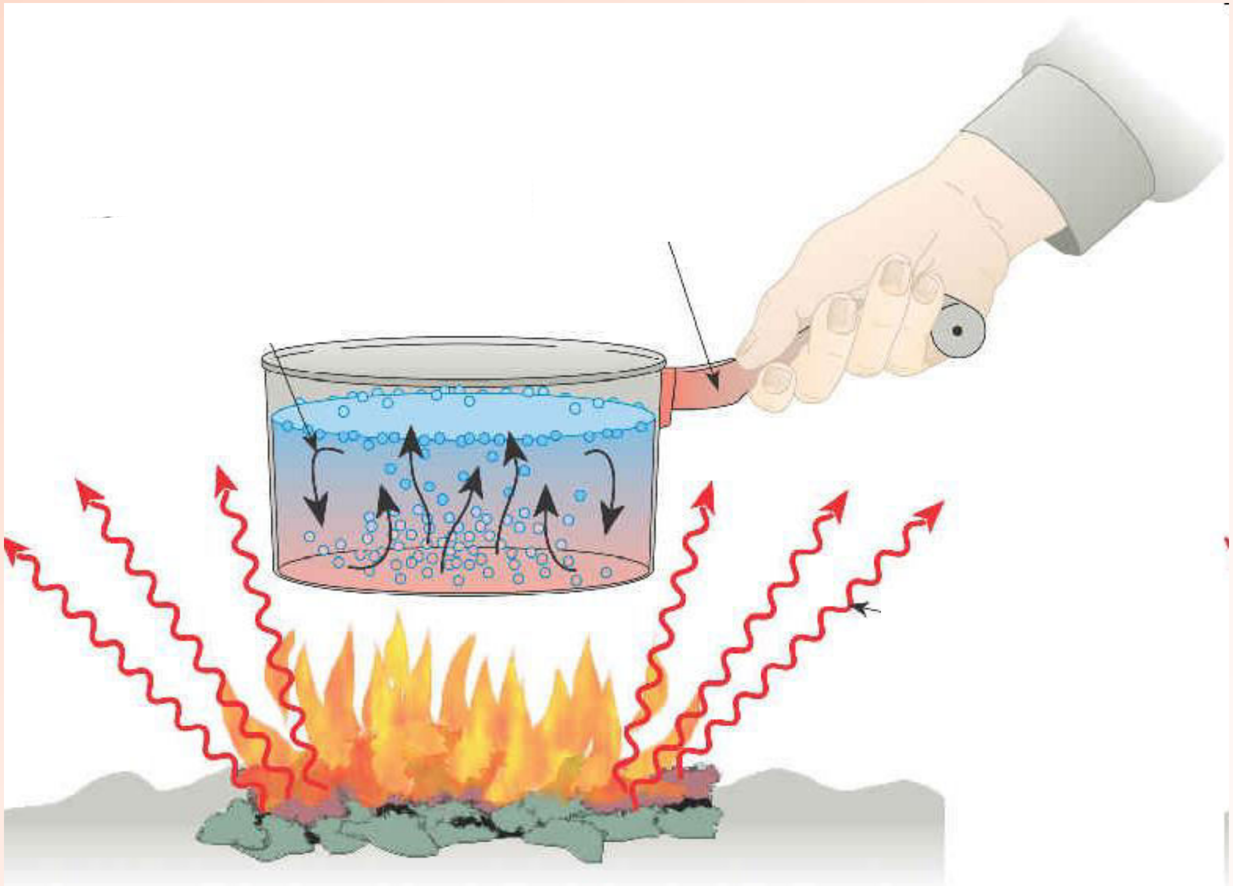


FIRST LAW OF THERMODYNAMICS

FIRST LAW OF THERMODYNAMICS

The total amount of energy in the universe is constant (conservation of energy).

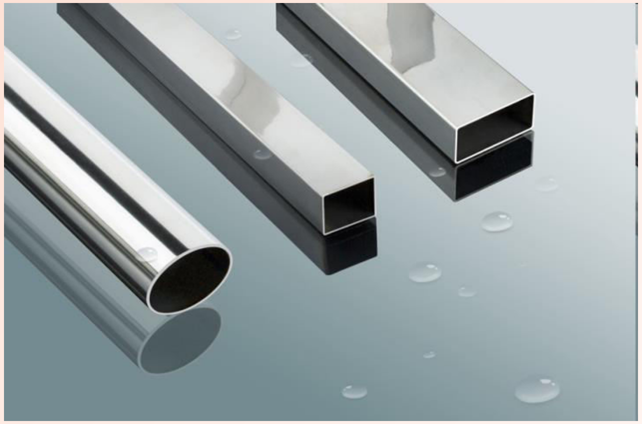
Energy is not created or destroyed.



SPECIFIC HEAT CAPACITY

Different types of matter require different amounts of heat transfer to change the same amount of temperature.

If provided the same amount of heat, which substance will feel the hottest?



Water is unusual in that it can absorb and release a lot of heat without the temperature changing drastically.

SPECIFIC HEAT CAPACITY

Specific heat capacity table:

TABLE 6.1 The Specific Heat Capacities of Some Common Substances

Substance	Specific Heat Capacity (J/°C · g)
$H_2O(l)$	4.18
$H_2O(s)$	2.03
$Al(s)$	0.89
$Fe(s)$	0.45
$Hg(l)$	0.14
$C(s)$	0.71

SPECIFIC HEAT CAPACITY

Specific Heat Capacity – the amount of heat transfer required to change the temperature of *one gram* of a substance one degree Celsius or Kelvin

$$c = q \,/\, m\Delta T$$

Specific heat capacity (J/g·^{o}C)

Quantity of heat transferred (J)

Mass (g)

Temperature (^{o}C)

Normally, you see the formula written as such: $q = mc\Delta T$

CALCULATIONS

Example 1: If a gold ring with a mass of 5.5 g changes in temperature from 25.0°C to 28.0°C, how much heat energy, in Joules, has it absorbed?

The value of the specific heat capacity of gold is 0.129 **J/(g·ºC)**.

Given:
$m = 5.5g$
$\Delta T = 28.0ºC - 25.0ºC = 3.0ºC$
$c = 0.129\ J/(g \cdot ºC)$

$$\begin{aligned} c &= q / m\Delta T \\ q &= mc\Delta T \\ &= (5.5g) \times (0.129\ J/g\cdot ºC) \times (3.0ºC) \\ &= 2.1285\ J \\ &= 2.1\ J \end{aligned}$$

Therefore the amount of heat absorbed is 2.1 J

CALCULATIONS

Example 2: What would be the final temperature if 250.0 J of heat were transferred into 10.0g of methanol ($c = 2.9$ J / g • °C) initially at 20. °C?

Given:
$m = 10.0g$
$\Delta T = x - 20^oC$
$c = 2.9$ J/(g·°C)

$$
\begin{aligned}
c &= q / m\Delta T \\
\Delta T &= q / mc \\
&= 250.0 \text{ J} / 10.0\text{g} \times 2.9 \text{ J/g}\cdot{}^oC \\
&= 8.62^oC \\
\\
\Delta T &= x - 20^oC \\
8.62^oC &= x - 20^oC \\
&= 28.62^oC \\
&= 29^oc
\end{aligned}
$$

Therefore the final temperature is 29°C

CALCULATIONS

Example 3: The temperature of a 250g sample of water is changed from 25.0°C to 30.0°C. How much energy was transferred into the water to cause this change? Calculate your answer in J, kJ, calories, and kilocalories. The heat capacity of water is 4.2J/g·°C

Let's analyze the question…

You're solving for q, but you don't know the following:

What is a kJ? 1kJ =1000J

What is a calorie? 1cal =4.2J

What is a kilocalorie? 1kcal =4200J or 4.2kJ

A calorie is the specific amount of heat required to raise the temperature of 1g of water by 1°C.

CALCULATIONS

Example 3: The temperature of a 250g sample of water is changed from 25.0°C to 30.0°C. How much energy was transferred into the water to cause this change? Calculate your answer in J, kJ, calories, and kilocalories. The heat capacity of water is 4.2J/g·°C

Given:

m = 250g

$\Delta T = 30.0^{\circ}C - 25.0^{\circ}C = 5.0^{\circ}C$

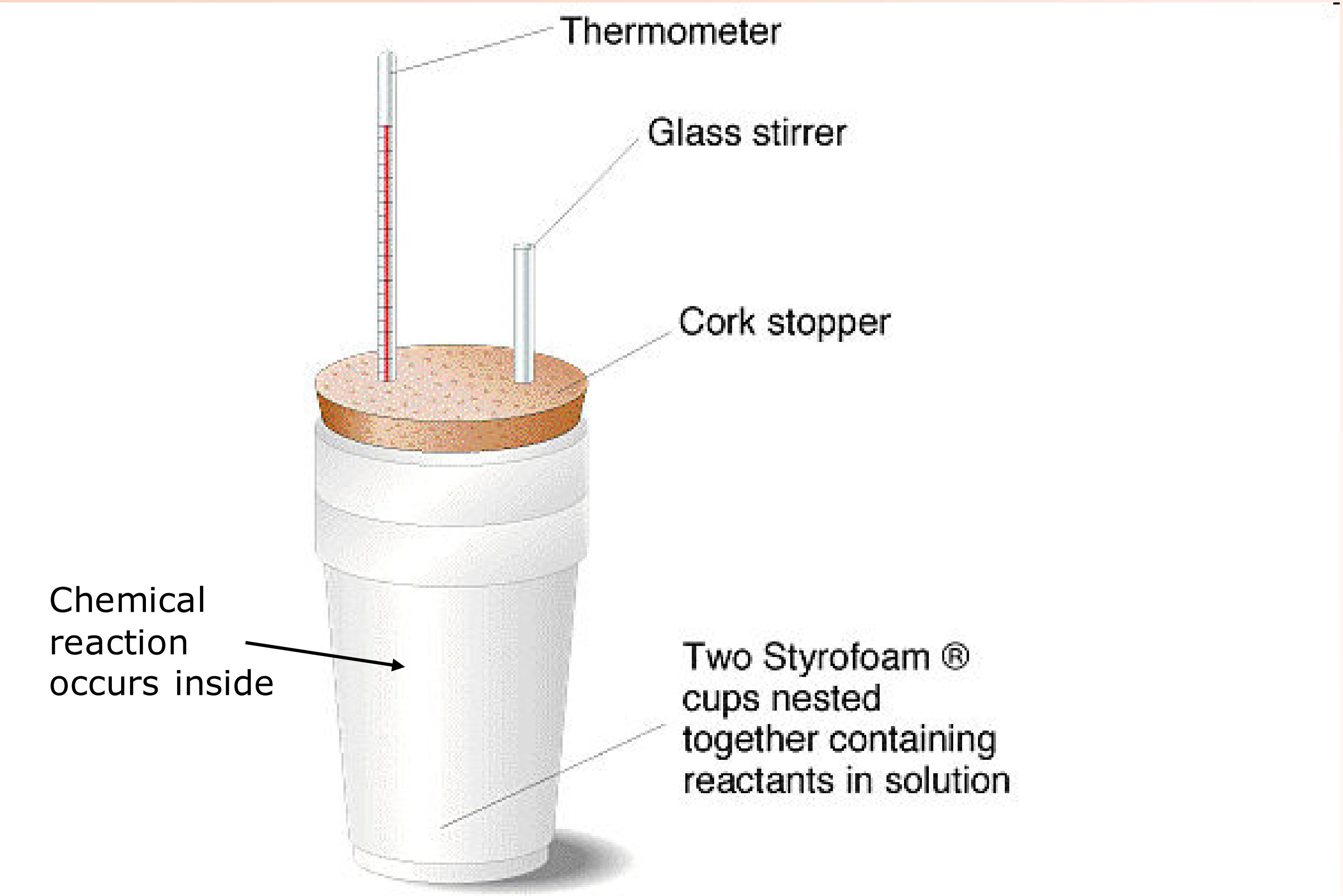
c = 4.2 J/g·°C

$$
\begin{aligned}
q &= mc\Delta T \\
&= (250g) \times (4.2\ J/g\cdot{}^{\circ}C) \times (5^{\circ}C) \\
&= 5250J \\
\\
&= 5250\ J \\
&= 5.25\ kJ \\
&= 1.25\ kcal \\
&= 1250\ cal
\end{aligned}
$$

Therefore the energy transferred into the water is 5.2×10^{3}J, 5.2kJ, 1.2kcal, and 1.2×10^{3}cal

CALORIMETRY

Calorimetry - the measure of heat change due to a chemical reaction



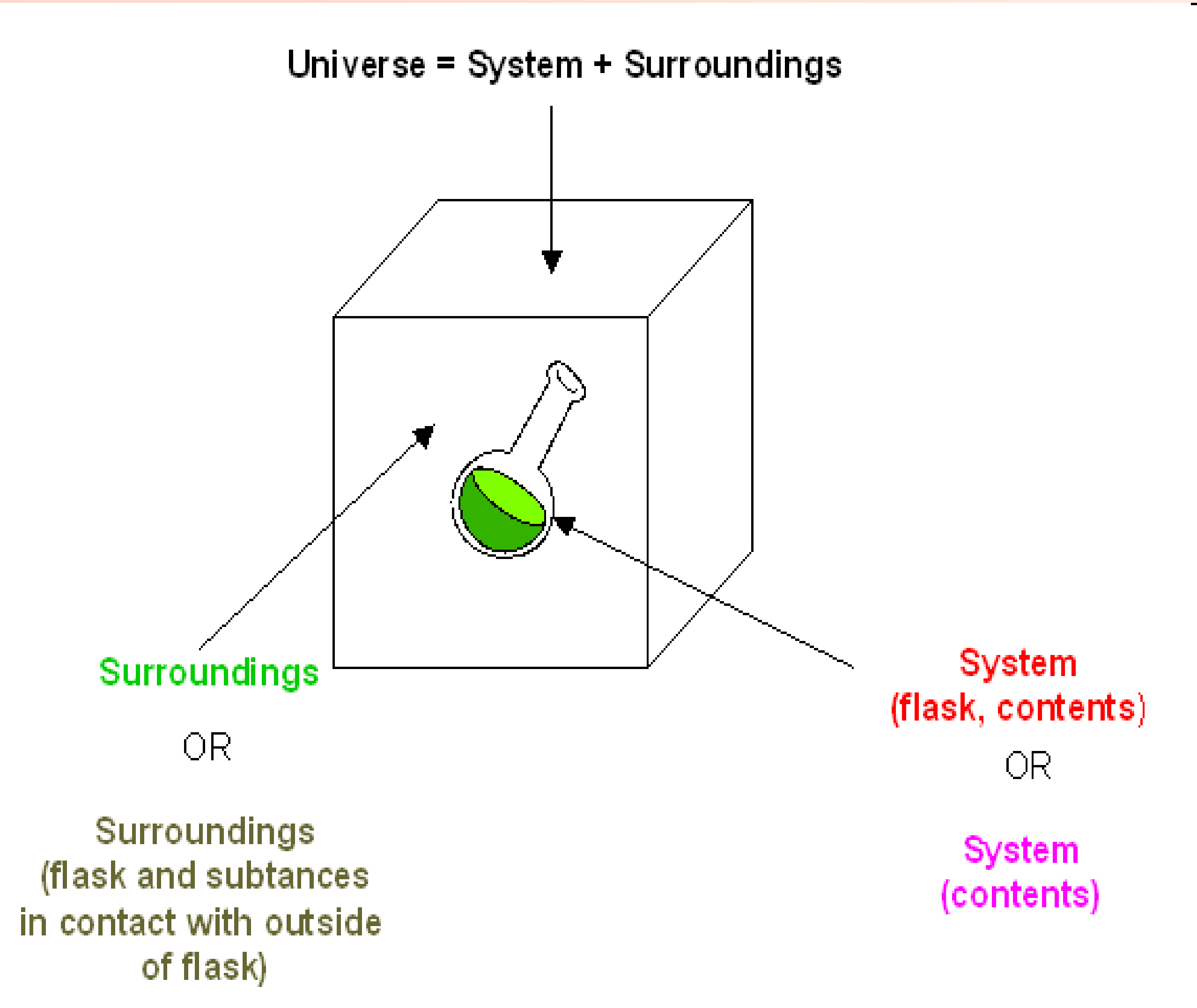
CALORIMETRY

Calorimetry

System – all objects that are being studied (usually the chemical reaction)

systems typically are defined by boundaries

Surroundings – all objects that are not the system



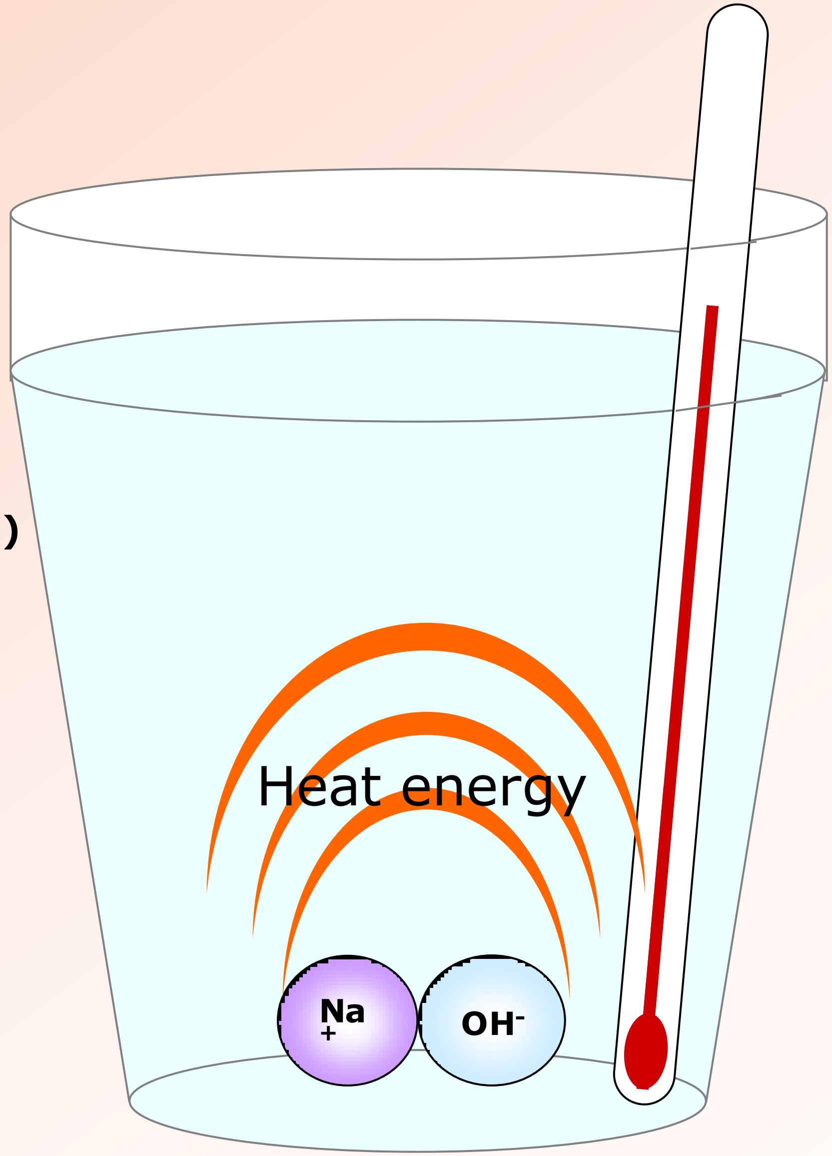
CALORIMETRY

System and Surroundings:

When solid NaOH is dissolved in water, heat energy is released.

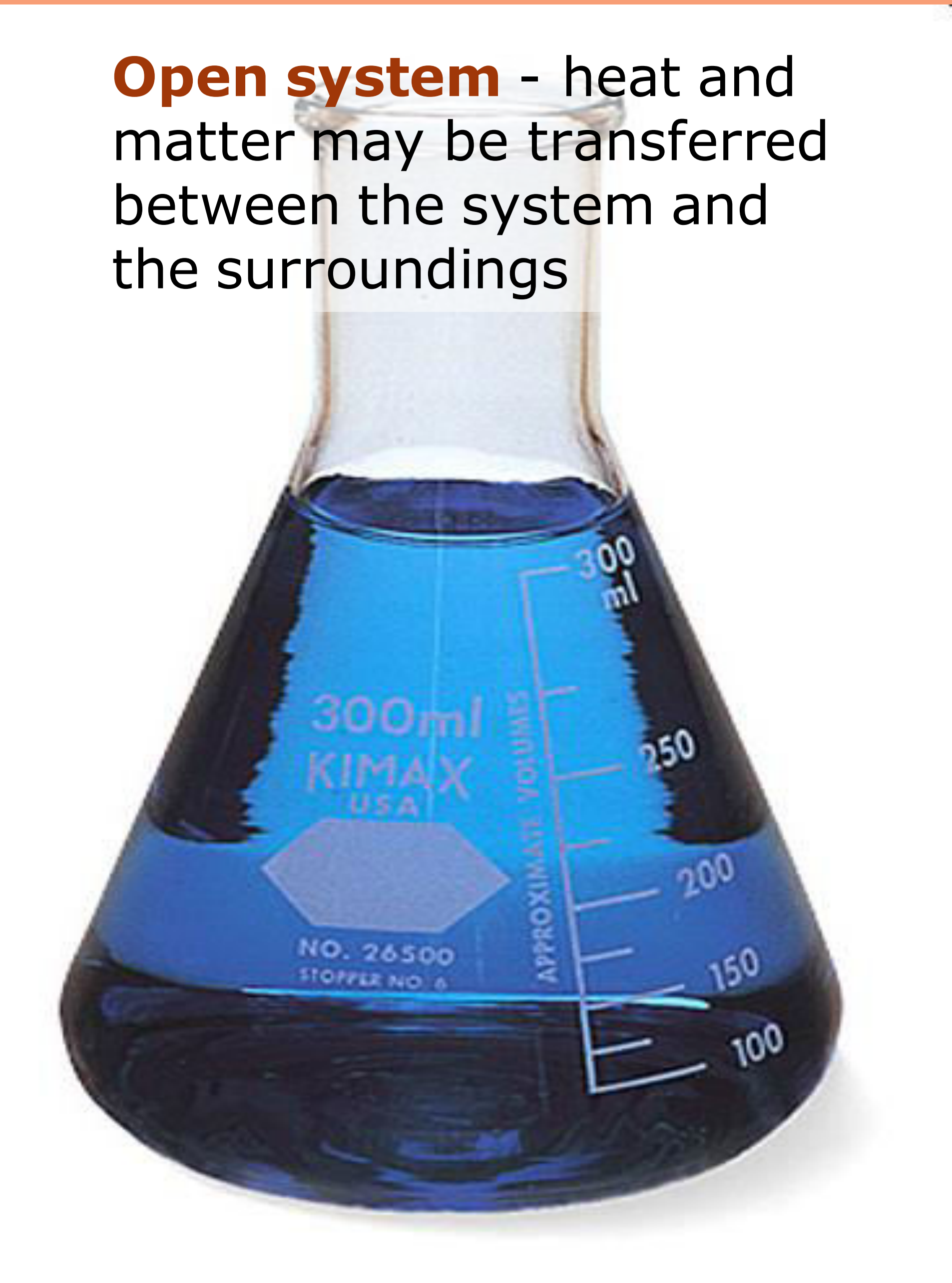
System: $\mathbf{NaOH_{(s)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}}$

Surroundings: **Water**



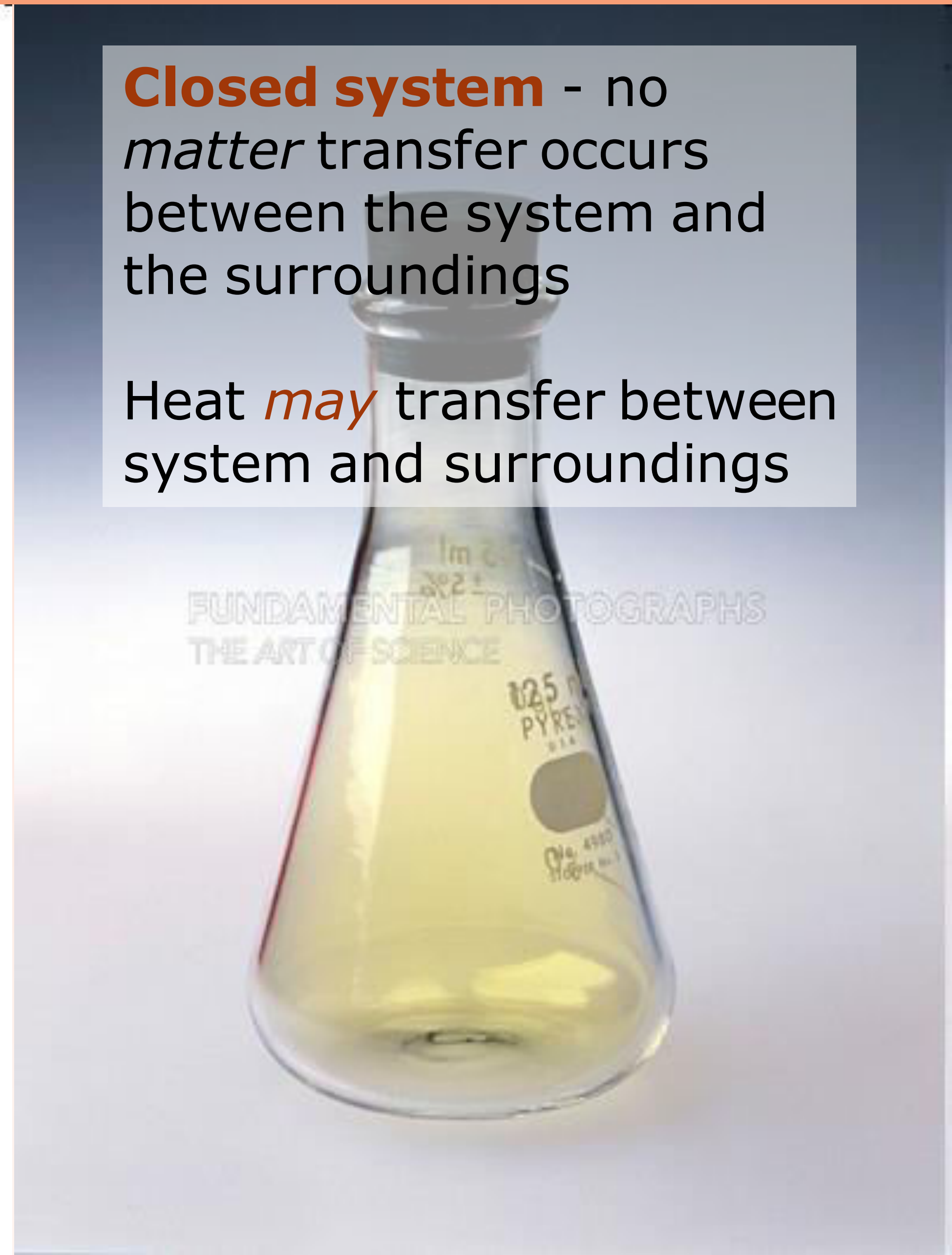
CALORIMETRY

Open system - heat and matter may be transferred between the system and the surroundings



Closed system - no *matter* transfer occurs between the system and the surroundings

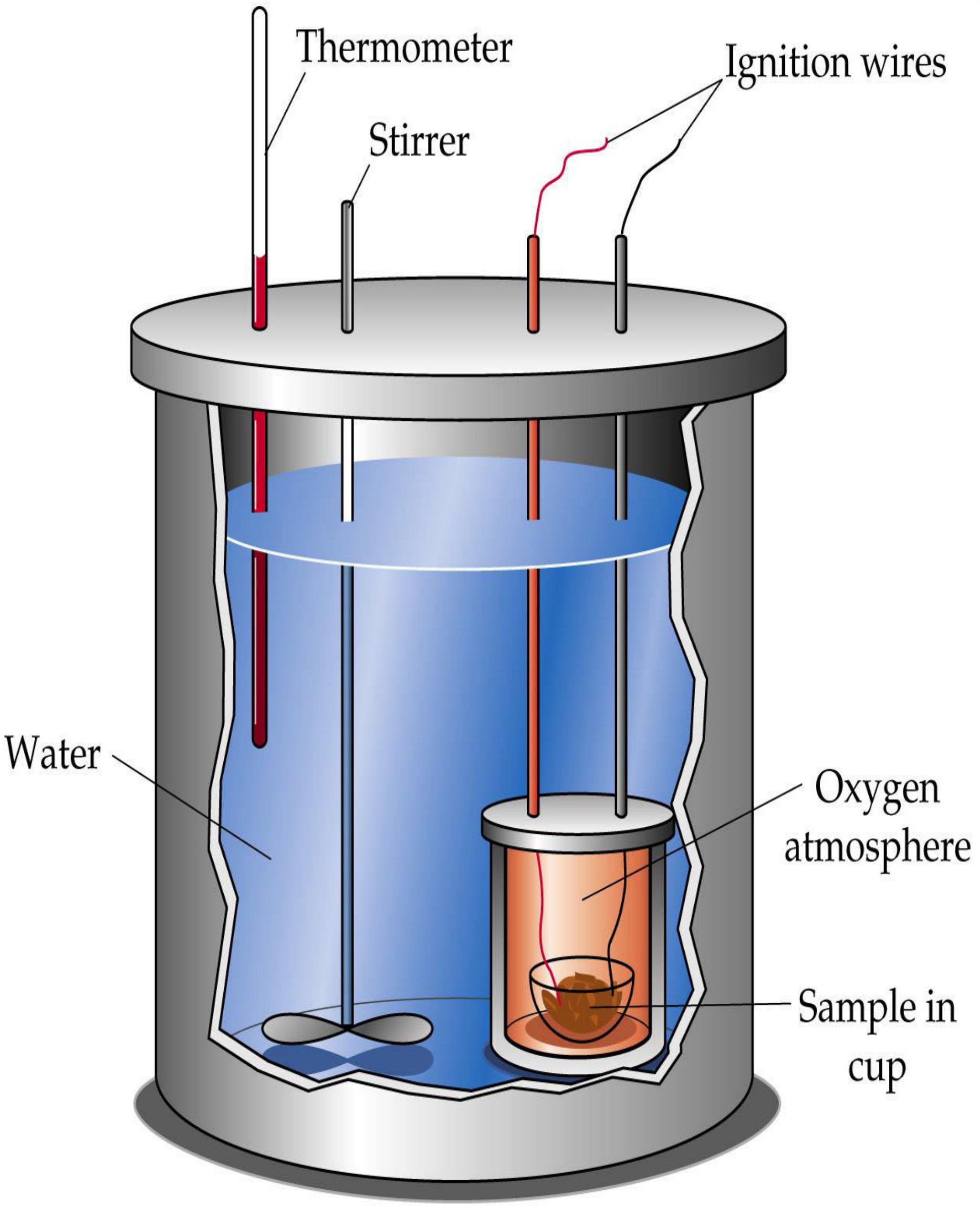
Heat *may* transfer between system and surroundings



CALORIMETRY

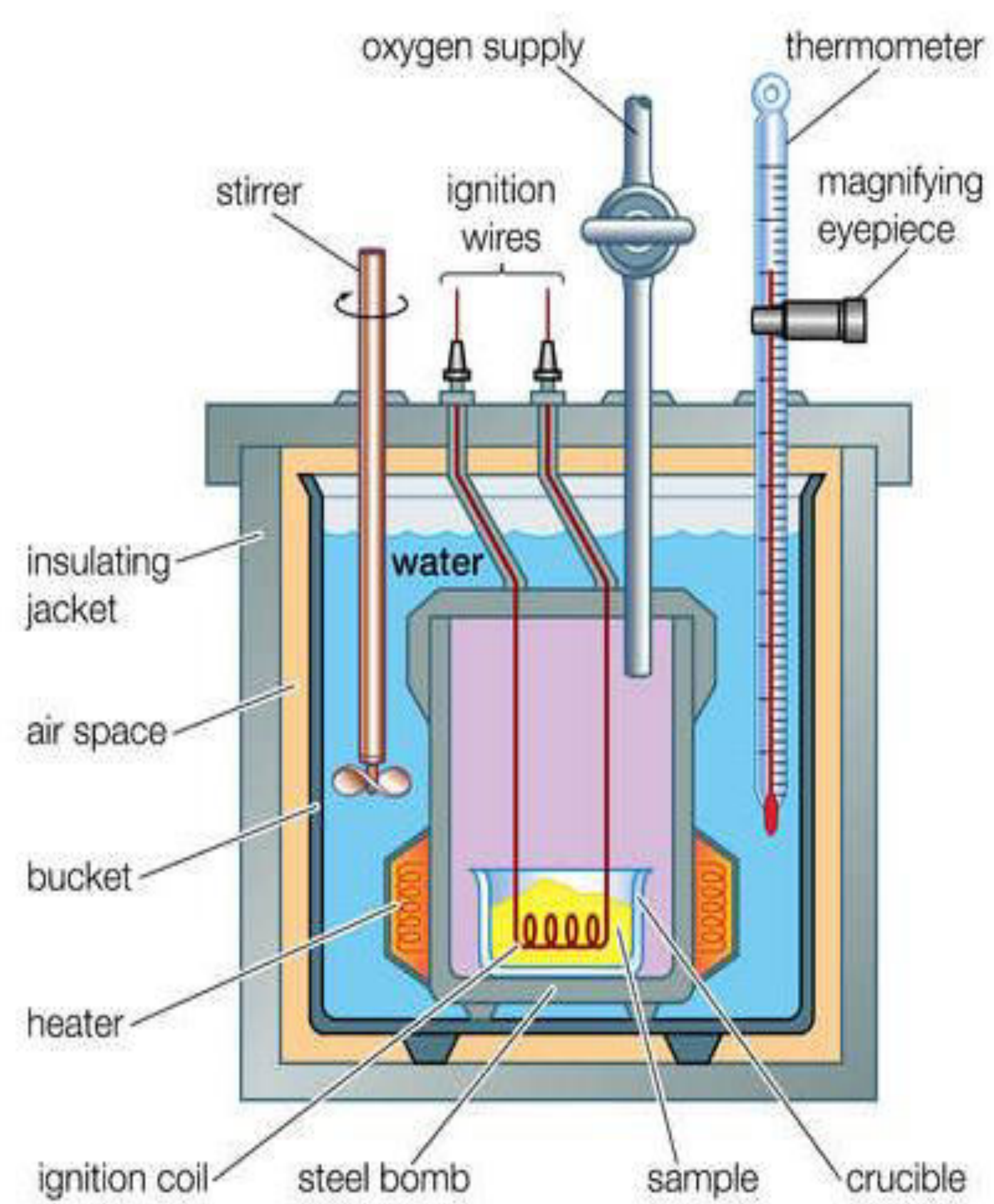
Isolated system – heat nor matter may transfer between the system and surroundings

This is the *ideal* system.



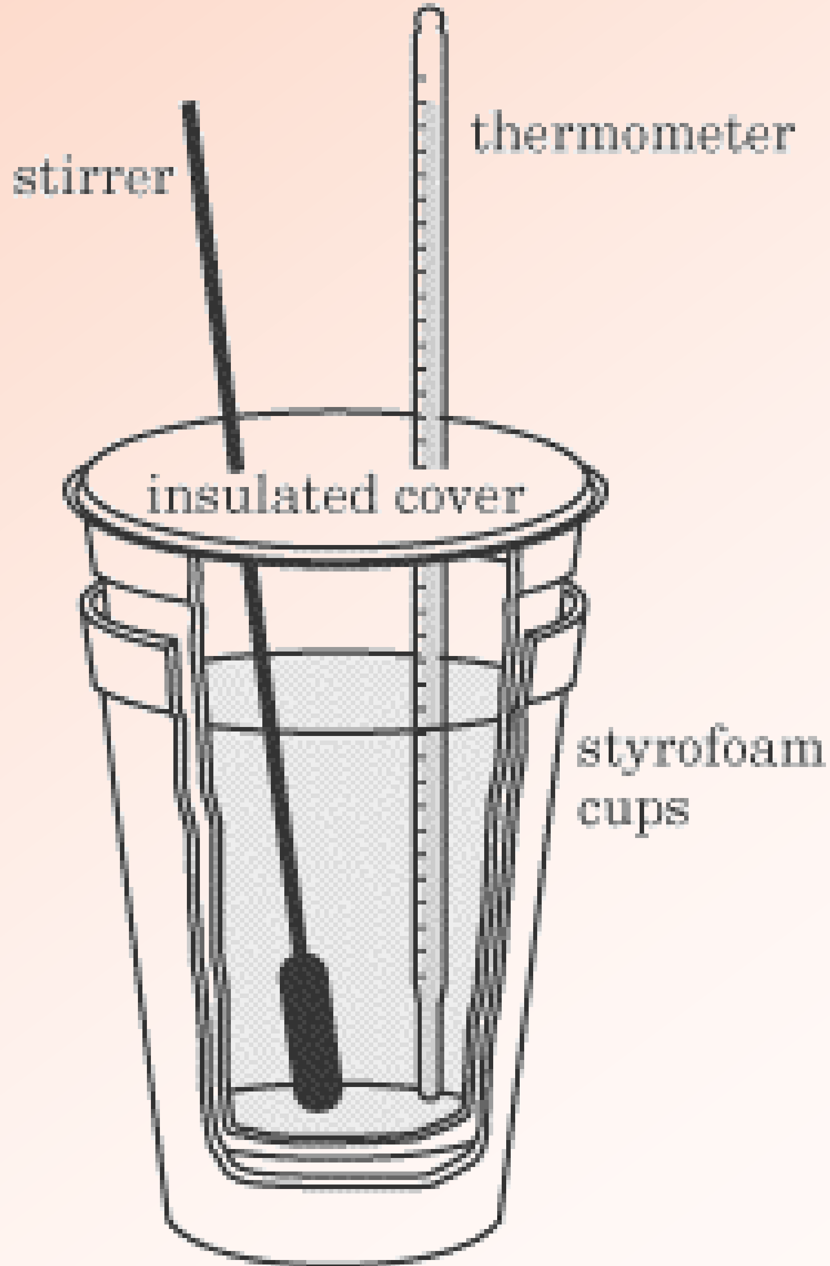
CALORIMETRY

Bomb calorimeter - reaction chamber allows heat transfer to the surrounding water, all contained within an insulated container



CALORIMETRY

Coffee cup calorimeter – styrofoam is not a conductor of heat, acting as insulation



EXOTHERMIC VS ENDOTHERMIC

Calorimetry

Exothermic reaction

– Reaction where the system releases heat to the surroundings
- ALL calculations involving these reactions will have a negative answer

Endothermic reaction

– Reaction where the system absorbs heat from the surroundings
- ALL calculations involving these reactions will have a positive answer

CALORIMETRY CALCULATIONS

Example 4: When 1.02g of steric acid, $C_{18}H_{36}O_2$, was burned completely in a bomb calorimeter, the temperature of the calorimeter rose by 4.26°C. The heat capacity of the calorimeter was 9.43 kJ/°C. Calculate the total heat of combustion of steric acid in kJ / mol.

This already takes into account the mass

Let's analyze the question…

Normally, we solve for the total change in heat. This time, we solve for the same thing, but PER MOLE. So we simply use the specific heat formula to solve for q, and divide the answer by the number of moles (n)

$$q = c\Delta T$$

Then, divide q by n $\quad \frac{q}{n} \leftarrow$ # of moles

CALORIMETRY CALCULATIONS

Example 4: When 1.02g of steric acid, $C_{18}H_{36}O_2$, was burned completely in a bomb calorimeter, the temperature of the calorimeter rose by 4.26°C. The heat capacity of the calorimeter was 9.43 kJ/°C. Calculate the total heat of combustion of steric acid in kJ / mol.

Given:

m = 1.02g

n = m/M

= 1.02g / (12.011 x 18 + 1.008 x 36 + 16.00 x 2)g/mol

= 1.02g / 284.486g/mol

= 0.003585414 mol

Why do we need to solve for moles?

Because this question is asking for q per mole

ΔT = 4.26°C

c = 9.43 kJ/°C

CALORIMETRY CALCULATIONS

Example 4: When 1.02g of steric acid, $C_{18}H_{36}O_2$, was burned completely in a bomb calorimeter, the temperature of the calorimeter rose by 4.26°C. The heat capacity of the calorimeter was 9.43 kJ/°C. Calculate the total heat of combustion of steric acid in kJ / mol.

Given:

m = 1.02g n = 0.003585414 mol ΔT = 4.26ºC c = 9.43 kJ/ºC

$$q = c\Delta T$$

$$= (9.43\ \text{kJ}/\text{º}\cancel{\text{C}}) \times (4.26\text{º}\cancel{\text{C}})$$

$$= 40.1718\text{kJ}$$

$$\frac{q}{n} = \frac{40.1718\text{kJ}}{0.003585414\text{mol}}$$

$$= 11204.23\ \text{kJ/mol}$$

CALORIMETRY CALCULATIONS

Example 4: When 1.02g of steric acid, $C_{18}H_{36}O_2$, was burned completely in a bomb calorimeter, the temperature of the calorimeter rose by 4.26°C. The heat capacity of the calorimeter was 9.43 kJ/°C. Calculate the total heat of combustion of steric acid in kJ / mol.

Given:

m = 1.02g   n = 0.003585414 mol   ΔT = 4.26ºC   c = 9.43 kJ/ºC

q = 11204.23 kJ/mol

Don’t forget scientific notation and significant digits!

= 1.12×10^4 kJ/mol

Don’t forget that this is an exothermic reaction!

= -1.12×10^4 kJ/mol

Therefore the total heat of combustion is -1.12×10^4 kJ/mol

CALORIMETRY CALCULATIONS

Example 5: 175g of water was placed in a coffee cup calorimeter and chilled to 10.°C. Then 4.90 g of sulfuric acid was added at 10.°C and the mixture was stirred. The temperature rose to 14.9°C. Assume the specific heat capacity of the water is 4.2 J/g •°C. Calculate the heat produced in kJ and the heat produced per mole of sulfuric acid.

Let's analyze the question…

The question is asking for q, but also q per mole. What "mole" is it referring to?

It's asking for q per mole of H_2SO_4. So you must solve for the moles of H_2SO_4.

CALORIMETRY CALCULATIONS

Example 5: 175g of water was placed in a coffee cup calorimeter and chilled to 10.°C. Then 4.90 g of sulfuric acid was added at 10.°C and the mixture was stirred. The temperature rose to 14.9°C. Assume the specific heat capacity of the water is 4.2 J/g •°C. Calculate the heat produced in kJ and the heat produced per mole of sulfuric acid.

Given:

$m = 175g$

$n = m/M$

$= 4.90g / (1.008 \times 2 + 32.065 \times 1 + 16.00 \times 4)g/mol$

$= 4.90g / 98.081g/mol$

$= 0.049958708\ mol$

$\Delta T = 14.9^oC - 10^oC = 4.9^oC$

$c = 4.2\ J/g \cdot {}^oC$

CALORIMETRY CALCULATIONS

Example 5: 175g of water was placed in a coffee cup calorimeter and chilled to 10.°C. Then 4.90 g of sulfuric acid was added at 10.°C and the mixture was stirred. The temperature rose to 14.9°C. Assume the specific heat capacity of the water is 4.2 J/g •°C. Calculate the heat produced in kJ and the heat produced per mole of sulfuric acid.

Given:

$m = 175g \quad n = 0.049958708 \text{ mol} \quad \Delta T = 4.9°C \quad c = 4.2 \text{ J/g·°C}$

$$q = mc\Delta T$$

$$= (175g) \times (4.2 \text{ J/g·°C}) \times (4.9°C)$$

$$= 3601.5 \text{ J}$$ ← This is your first answer!

$$\frac{q}{n} = \frac{3601.5 \text{ J}}{0.049958708 \text{mol}}$$

$$= 72089.5344 \text{ J/mol}$$

$$= 72 \text{ kJ/mol}$$ ← This is your second answer!

CALORIMETRY CALCULATIONS

Example 5: 175g of water was placed in a coffee cup calorimeter and chilled to 10.°C. Then 4.90 g of sulfuric acid was added at 10.°C and the mixture was stirred. The temperature rose to 14.9°C. Assume the specific heat capacity of the water is 4.2 J/g •°C. Calculate the heat produced in kJ and the heat produced per mole of sulfuric acid.

Given:

m = 175g n = 0.049958708 mol ΔT = 4.9ºC c = 4.2 J/g·ºC

$$q = 3601.5702.342\ J$$
$$= 3.6kJ$$

$$\frac{q}{n} = 72kJ/mol$$

Remember that this is an exothermic reaction!!

Therefore the heat of reaction is -3.6kJ and the heat per mole of sulfuric acid is -72kJ/mol

CALORIMETRY CALCULATIONS

Example 6: The reaction of HCl and NaOH is exothermic. A student placed 50.0 mL of 1.00 M HCl at 25.5°C in a coffee cup calorimeter and then added 50.0 mL of 1.00 M NaOH also at 25.5°C. The mixture was stirred and the temperature quickly increased to 32.4°C. What is the heat of the reaction in J/mol of HCl? The heat capacity of H_2O is 4.2 J/g•°C. , and its density is 1.00g/mL.

Let's analyze the question…

The reaction that occurs is

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(l)} + NaCl_{(aq)} + \text{energy}$$

Since we have equal volumes of both, then the total volume is 100.0mL. With a density of 1.00g/mL, the mass of the water is 100.0g.

Once again, we are solving for q, but per mole.

CALORIMETRY CALCULATIONS

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Given:

m = 100.0g

c = 4.2 J/g•°C

ΔT = 32.4°C-25.5°C = 6.9°C

n_{HCl} = CV
= 1.00M x 0.0500L ← Remember to convert mL to litres
= 0.0500mol

CALORIMETRY CALCULATIONS

Example 6: The reaction of HCl and NaOH is exothermic. A student placed 50.0 mL of 1.00 M HCl at 25.5°C in a coffee cup calorimeter and then added 50.0 mL of 1.00 M NaOH also at 25.5°C. The mixture was stirred and the temperature quickly increased to 32.4°C. What is the heat of the reaction in J/mol of HCl? The heat capacity of H_2O is 4.2 J/g•°C, and its density is 1.00g/mL.

Given:

m = 100.0g   c = 4.2 J/g•°C ΔT = 6.9°C n_{HCl} = 0.0500mol

$$q = mc\Delta T$$

$$= (100.0g) \times (4.2\ J/g\cdot{}^oC) \times (6.9^oC)$$

$$= 2898J$$

$$\frac{q}{n} = \frac{2898J}{0.0500mol}$$

$$= 57960J/mol$$

$$= -5.8\times10^4 J/mol$$

Therefore the heat of the reaction is -5.8×10^4J/mol of HCl

CALORIMETRY CALCULATIONS

Example 7: A sample of 2.65 g of carbon in the form of graphite was burned in oxygen in a bomb calorimeter. The temperature of the calorimeter increased from 22.25^{o}C to 30.55^{o}C. The calorimeter itself is made of 3.000 kg of lead (c lead= 300 J/g^{o}C) and contains 2000.0 mL of water (4.18 J/ g^{o}C). Determine the molar enthalpy of this sample of carbon's combustion.

Let's analyze the question…

What are the two components of the calorimeter? How does this affect the heat capacity of the calorimeter?

CALORIMETRY CALCULATIONS

Example 7: A sample of 2.65 g of carbon in the form of graphite was burned in oxygen in a bomb calorimeter. The temperature of the calorimeter increased from 22.25°C to 30.55°C. The calorimeter itself is made of 3.000 kg of lead (c lead= 300 J/g°C) and contains 2000.0 mL of water (4.18 J/ g°C). Determine the molar enthalpy of this sample of carbon's combustion.

Given:

$\Delta T = 30.55°C – 22.25°C = 8.3°C$

$m_{calorimeter} = 3000.g + 2000.0g = 5000.g$

m% of the calorimeter: 60% lead, 40% water

$c_{calorimeter} = 60\% \times 300 J/g°C + 40\% \times 4.18 J/g°C$
$= 181.672 J/g°C$ ← specific heat capacity

OR

$c_{calorimeter} = 3000.g \times 300 J/g°C + 2000.0g \times 4.18 J/g°C$
$= 908360 J/°C$ ← heat capacity

CALORIMETRY CALCULATIONS

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Given:

$\Delta T = 8.3^{o}C$

$m_{calorimeter} = 5000.g$

$C_{calorimeter} = 908360 J/^{o}C$

$$
\begin{aligned}
n &= m/M \\
&= 2.65g / 12.011g/mol \\
&= 0.220631088mol
\end{aligned}
$$

CALORIMETRY CALCULATIONS

Calorimetry

Example 7: A sample of 2.65 g of carbon in the form of graphite was burned in oxygen in a bomb calorimeter. The temperature of the calorimeter increased from 22.25°C to 30.55°C. The calorimeter itself is made of 3.000 kg of lead (c lead= 300 J/g°C) and contains 2000.0 mL of water (4.18 J/ g°C). Determine the molar enthalpy of this sample of carbon's combustion.

Given:

$\Delta T = 8.3^oC$ $\quad c_{calorimeter} = 908360 J/^oC$ $\quad n = 0.220631088 mol$

$$
\begin{aligned}
q &= c\Delta T \\
&= (908360 J/^oC) \times (8.3^oC) \\
&= 7539388\ J
\end{aligned}
$$

$$
\begin{aligned}
\frac{q}{n} &= \frac{7539388\ J}{0.220631088 mol} \\
&= 34171920.5 J/mol \\
&= -3.42\times10^4 KJ/mol
\end{aligned}
$$

Therefore the molar enthalpy is $-3.42\times10^4 kJ/mol$

CALORIMETRY CALCULATIONS

Example 8: How much water at 100.0 ºC must be added to 80.0 g of water at 25.0 ºC to give a final temperature of 85.0 ºC? (3 marks; T/I)

Given:

Water @ 25°C
m=80.0g
c=4.2J/g°C
ΔT=85°C-25°C
=60°C

$q_{lost} = q_{gained}$

Water @ 100°C
m= ?
c=4.2J/g°C
ΔT=85°C-100°C
=-15°C

$q_{gained} = mc\Delta T$

$= (80.0g) \times (4.2\ J/g\cdot{}^{o}C) \times (60^{o}C)$

$= 20160J$

$= q_{lost}$

$q_{lost} = mc\Delta T$

$m = \frac{q_{lost}}{c\Delta T}$

$m = -\frac{20160}{4.2 \times -15}$

$m = 320g$

$.\!: m = 3.2 \times 10^{2}g$

CALORIMETRY CALCULATIONS

Example 8: How much water at 100.0 ºC must be added to 80.0 g of water at 25.0 ºC to give a final temperature of 85.0 ºC? (3 marks; T/I)

Given:

T_f = 85ºC T_1= 25ºC, m_1=80.0g T_2= 100ºC, m_2=**x**

$$\frac{80.0}{80.0+x} \times 25^{o}C \quad + \quad \frac{x}{80.0+x} \times 100^{o}C \quad = \quad 85^{o}C$$

$$2000 \quad + \quad 100x \quad = \quad 6800 + 85x$$

$$15x = 4800$$

$$x = 320g$$

Therefore 320g of water must be added