# Calorimetry

In the laboratory, heat changes in physical and chemical processes are measured with a calorimeter which is a closed container designed specifically for this purpose.

The measurement of heat changes will depend on specific heat and heat capacity.

The specific heat (s) → of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius . It has the units J/g .°C

The heat capacity (C) → of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius. Its units are J/°C .

Specific heat is an intensive property whereas heat capacity is an extensive property .

The relationship between the heat capacity and specific heat of a substance is $c = m\,s$

Where m is the mass of the substance in grams.

"Example"

If the specific heat of 60g of water is 4.18J/g

If we know the specific heat and the amount of a substance, then the change in the sample's temperature ($\Delta t$ ) will tell us the amount of heat (q) that has been absorbed in or released in a particular process. The equations for calculating the heat change are given by

معادله لحساب التغير الحرارى .

$$q = ms\Delta t \qquad (12)$$

$$q = C\Delta t \qquad (13)$$

Where $\Delta t$ is the temperature change:

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

The sign for q is the same as that for enthalpy change ;q is positive for endothermic processes and negative for exothermic processes.

Solution

$C = m S$

$= 60 * 4.18 = 251 \text{ J/}^{o}\text{C}$

# Calorimetry

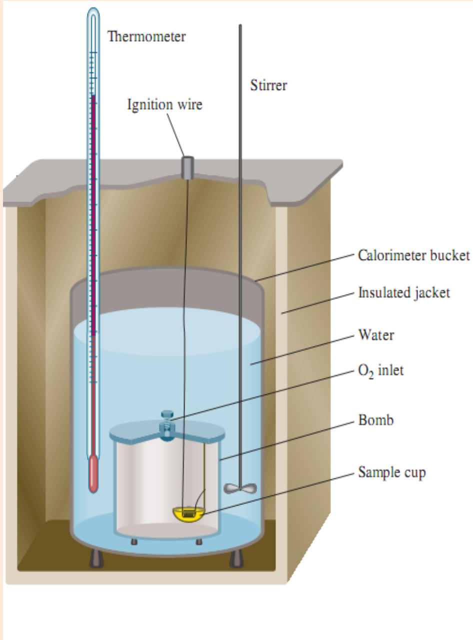
Constant-Volume Calorimetry

Constant-pressure Calorimetry

## 1) Constant volume calorimetry

* Is used for measuring heat of combustion by placing a Known mass of a compound in a steel container called "constant volume bomb calorimeter".

### Composition




- The bomb is filled with oxygen

at about 30 atm of pressure.

- The closed bomb is immersed in

a known amount of water.

- The sample is ignited electrically.

The heat produced by the combustion reaction can be calculated accurately by recording the rise in temp of water.

- The heat given off the sample

is absorbed by the water and bomb.

Note that:

The special design of the calorimeter enables us to assume that, no heat is lost to the surroundings during the time it takes to make measurements.

- We can call the bomb and the water in which it submerged an isolated system.
- The heat change of the system ($q_{system}$) must be zero?? why

Because no heat enters or leaves the system through the process.

$$q_{system} = q_{cal} + q_{rxn} = 0$$

$q_{cal}$ → heat changes for calorimeter.

$q_{rxn}$ → heat changes for reaction.

$$q_{cal} = - q_{rxn}$$

$$q_{cal} = - C_{cal}\,\Delta t$$

For example

It is known that the combustion of 1 g of benzoic acid ($C_6H_5COOH$) releases 26.42 kJ of heat. If the temperature rise is 4.6738C, then heat capacity of the calorimeter is given by

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

$= 26.42\ kj/4.673°c$ =5.654 kJ/°C

Once C cal has been determined, the calorimeter can be used to measure the heat of combustion of other substances.

Note that → because reactions in a bomb calorimeter occur under constant-volume rather than constant-pressure conditions, the heat changes do not correspond to the enthalpy change ΔH.

$$q_{Sys} = q_{water} + q_{bomb} + q_{reaction}$$

$$q_{Sys} = 0$$

$$q_{reaction} = -(q_{water} + q_{bomb})$$

$$q_{water} = m\ S\ \Delta t\ ,\ q_{bomb} = C_{bomb}\ \Delta t$$

## Constant-Pressure Calorimetry

A simpler device than the constant-volume calorimeter is the constant-pressure calorimeter.

Which is used to determine the heat changes for non-combustion reactions?

As shown in Figure. This device measures the heat effects of a variety reactions, such as acid-base neutralization, as well as the heat of of dilution. Because the pressure is constant, the heat solution and heat of equal to the enthalpy change (ΔH). As in change for the process ($q_{rxn}$) is the case of a constant-volume calorimeter.

We treat the calorimeter as an isolated system.

$q_{Sys} = q_{water} + q_{Cal} + q_{rxn}$

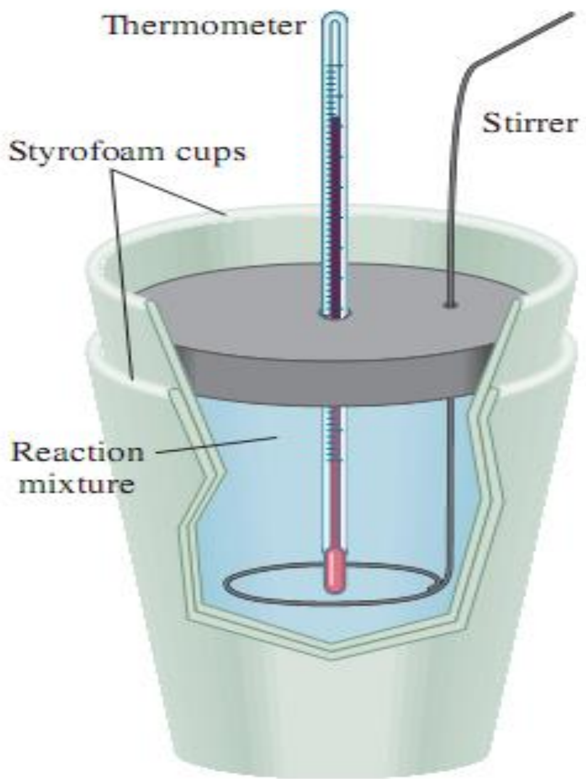
$q_{sys} = 0$

$q_{rxn} = -(q_{water} + q_{Cal})$

$q_{water} = m\,S\,\Delta t$ , $q_{Cal} = C_{Cal}\,\Delta t$

Reaction at constant P

$\Delta H = q_{rxn}$



## Questions

**1.** A quantity of 1.435 g of naphthalene ($C_{10}H_8$), . was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 20.28°C to 25.95°C. If the heat capacity of the bomb plus water was 10.17 kJ/°C, calculate the heat of combustion of naphthalene on a molar basis; that is, find the molar heat of combustion.

**Solution**

The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change. Assuming no heat is lost to the surroundings, we write

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

$$= (10.17 kJ/°C)\ (25.95°C - 20.28°C)$$

$$= 57.665\ kJ.$$

Because $q_{sys} = q_{cal} + q_{rxn} = 0,$ $q_{cal} = - q_{rxn}.$

The heat change of the reaction is -57.66 kJ

This is the heat released by the combustion of 1.435 g of $C_{10}H_8$ ;

therefore, we can write

$C_{10}H_8$ ........................................ heat

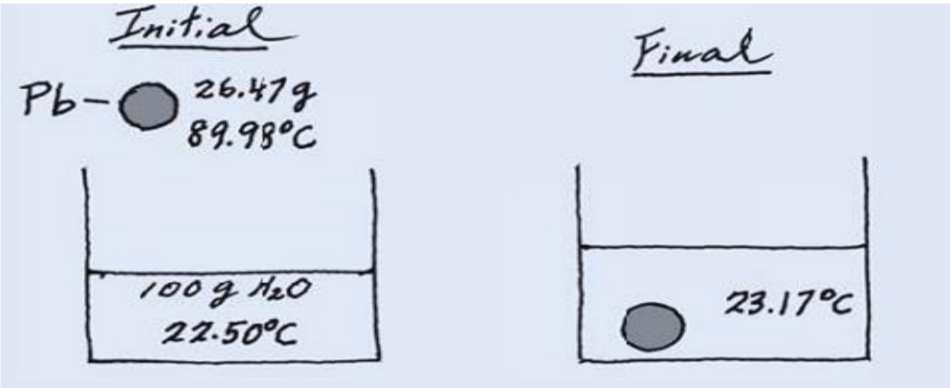
1.435 g ........................................ 57.66 kJ

128.2 g(1mole) ........ .................. x kJ

$$X = \frac{57.66 \times 128.2}{1.435} = 5.151 \times 10^3 kJ \therefore mole$$

2- A lead (Pb) pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat of the lead pellet?

**Strategy**




A sketch of the initial and final situation .

**Solution**

Treating the calorimeter as an isolated system

(no heat lost to the surrounding we write)

$q_{Pb} + q_{H2O} = 0$ , or $q_{Pb} = -q_{H2O}$

The heat gained by the water is given by $q_{H2O} = ms\Delta t$

.$q_{H2O}$ = (100.0 g) (4.184 J/g. °C) (23.17°C - 22.50°C) =280.3 J

Because the heat lost by the lead pellet is equal to the heat gained by the water, so

$q_{Pb}$ = -280.3 J= $ms\Delta t$

-280.3 J = (26.47 g) (s) (23.17°C - 89.98°C)

s =0.158 J/g. ° C

**3.** A quantity of 100 mL of 0.500 M HCl was mixed with 100 mL of 0.500 M NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same, 22.50°C, and the final temperature of the mixed solution was 25.86°C.

Calculate the heat change for the neutralization reaction on a molar basis NaOH (aq) +HCl (aq) → NaCl (aq) + H2O (l)

Assume that the densities and specific heats of the solutions are the same as for water (1.00 g/mL and 4.184 J/g. °C, respectively).

Solution

Assuming no heat is lost to the surroundings, $q_{sys} = q_{soln} + q_{rxn} = 0$, so $q_{rxn} = - q_{soln}$ ,

where $q_{soln}$ is the heat absorbed by the combined solution. Because the density of the solution is 1.00 g/mL, the mass of a 100-mL solution is 100 g .

Thus, $q_{soln} = ms\Delta t$

= (200g) (4.184 J/g. °C) (25.86°C - 22.50°C)

$=2.81*10^3 J = 2.81$ kJ

Because $q_{rxn} = - q_{soln}$ , $q_{rxn}$ =-2.81 kJ .

From the molarities given, the number of moles of both HCl and NaOH in $1.00*10^2$ mL solution is

$$\frac{0.500\text{mol}}{1l} *0.100\text{L} =0.0500 \text{ mol}$$

Therefore, the heat of neutralization when 1.00 mole of HCl reacts with 1.00 mole of NaOH is Heat of neutralization

= -2.81 kJ/0.0500 mol = -56.2 kJ/mol

Choose

1) An endothermic reaction causes the surroundings to

A) warm up

B) become acidic.

C) Condense.

D) decrease in temperature

2) An exothermic reaction causes the surroundings to

A) warm up

B) become acidic

C) expand

D) decrease its temperature

3) Copper metal has a specific heat of 0.385 J/g·°C. Calculate the amount of heat required to raise the temperature of 22.8 g of Cu from 20.0°C to 875°C.

A) $1.97 \times 10^{-5}$ J

B) $1.0 \times 10^{-2}$ J

C) 329 J

D) 7.51 kJ

Solution

$q = m\ s\ \Delta t$

$= 22.8 * 0.385 *(875-20) = 7505$ J

$=7.51$KJ

4) Calculate the amount of heat necessary to raise the temperature of 12.0 g of water from 15.4°C to 93.0°C. The specific heat of water = 4.18 J/g·°C.

A) 0.027 J
C) 389 J
B) 324 J
D) <u>3,890 J</u>

Solution

q = m s Δt

= 12 * 4.18 *(93-15.4) = 3892 J

=3.892KJ



6) How many degrees of temperature rise when a 25.0 g block of aluminum absorbs 10.0 kJ of heat? The specific heat of Al is 0.900 J/g·°C.

A) 0.44°C
C) 225°C
B) 22.5°C
D) <u>444°C</u>

Solution

q = m s Δt

$\Delta t = \frac{q}{mS}$

$= \frac{10 * 1000}{25 * 0.900} = 444°C$

7) If 325 g of water at 4.2°C absorbs 12.28 kJ, what is the final temperature of the water? The specific heat of water is 4.184 J/g·°C.

A) 4.21°C

B) 4.8°C

C) 9.0°C

D) 13.2°C

Solution

q = m s Δt

$$\Delta t = \frac{q}{mS} = \frac{12.28*1000}{325*4.184} = 9.03°C$$

$$\Delta t = tf - ti$$

$$tf = \Delta t + ti = 9.03 + 4.2 = 13.2°C$$

8) A glass containing 200. g of $H_2O$ at 20°C was placed in a refrigerator. The water loses 11.7 kJ as it cools to a constant temperature. What is its new temperature? The specific heat of water is 4.184 J/g·°C.

A) 0.013°C

B) 4°C

C) 6°C

D) 14°C

Solution

q = m s Δt

$$\Delta t = \frac{q}{mS} = \frac{-11.7*1000}{200*4.184} = -13.9°C$$

$$\Delta t = tf - ti$$

$$tf = \Delta t + ti = 20 + (-13.9) = 6.1°C$$

9) A piece of copper with a mass of 218 g has a heat capacity of 83.9 J/°C. What is the specific heat of copper?

A) 0.385 J/g·°C
C) 2.60 J/g·°C
B) $1.83 \times 10^4$ J/g·°C
D) 1.32 J/g·°C

Solution

C = m s

$$S = \frac{c}{m} = \frac{83.9}{218} = 0.38°L/g°C$$

10) The specific heat of gold is 0.129 J/g·°C. What is the molar heat capacity of gold?

A) 0.039 J/mol·°C
C) 25.4 J/mol·°C
B) 0.129 J/mol·°C
D) 39.0 kJ/mol·°C

Solution

C = m s

$$= 0.129 * 197 = \frac{25.4J}{mol°C}$$

11) Suppose a 50.0 g block of silver (specific heat = 0.2350 J/g·°C) at 100°C is placed in contact with a 50.0 g block of iron (specific heat = 0.4494 J/g·°C) at 0°C, and the two blocks are insulated from the rest of the universe. The final temperature of the two blocks

A) will be higher than 50°C

B) will be lower than 50°C

C) will be exactly 50°C

D) cannot be predicted

Solution

$M_I$ =50g $S_I$ =0.2350 J/g. °C $t_I$=100°C

$M_S$=50g $S_S$=0.4494 J/g. °C $t_S$=0 °C

$q_{sys} = q_{i+}q_s$

$q_{sys} = 0$

$q_i = -q_s$

$ms\Delta t = ms\Delta t$ , $50*0.2350*(t_f - 100) = 50*0.449*(t_f - 0)$

$0.2350t_f - 23.5 = -0.449t_f$

$T_f = 34.35°C$

13) Naphthalene combustion can be used to calibrate the heat capacity of a bomb calorimeter. The heat of combustion of naphthalene is -40.1 kJ/g. When 0.8210 g of naphthalene was burned in a calorimeter containing 1,000. g of water, a temperature rise of 4.21°C was observed. What is the heat capacity of the bomb calorimeter excluding the water?

A) 32.9 kJ/°C
B) 7.8 kJ/°C
C) 3.64 kJ/°C
D) 1.76 kJ/°C

14) Which of these processes is endothermic?

A) $O_2(g) + 2H_2(g) \rightarrow 2H_2O(g)$
B) $H_2O(g) \rightarrow H_2O(l)$
C) $3O_2(g) + 2CH_3OH(g) \rightarrow 2CO_2(g) + 2H_2O(g)$
D) H2O(s) → H2O(l)

15) A 100. mL sample of 0.200 M aqueous hydrochloric acid is added to 100. mL of 0.200 M aqueous ammonia in a calorimeter whose heat capacity (excluding any water) is 480. J/K. The following reaction occurs when the two solutions are mixed.

$$HCl_{(aq)} + NH_{3(aq)} \rightarrow NH_4Cl_{(aq)}$$

The temperature increase is 2.34°C. Calculate ΔH per mole of HCl and $NH_3$ reacted.

A) 154 kJ/mol
B) 1.96 kJ/mol
C) -154 kJ/mol
D) -1.96 kJ/mol

16) A 0.1326 g sample of magnesium was burned in an oxygen bomb calorimeter. The total heat capacity of the calorimeter plus water was 5,760 J/°C. If the temperature rise of the calorimeter with water was 0.570°C, calculate the enthalpy of combustion of magnesium.

$$Mg_{(s)} + 1/2O_{2(g)} \rightarrow MgO_{(s)}$$

A) -3280 kJ/mol

B) -24.8 kJ/mol

C) 106 kJ/mol

D) -602 kJ/mol

17) specific heat is

A) The amount of heat required to raise the temperature of one gram of a substance by one degree Celsius.

B) Any process that gives off heat to the surroundings.

C) is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius

D) all of the above

18) Heat capacity is

A) The amount of heat required to raise the temperature of one gram of a substance by one degree Celsius

B) Any process that gives off heat to the surroundings.

C) Is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius.

D) None of them