

Experiment no. 6:

Objective: *Determine the water equivalent of calorimeter.*

Theory: The water equivalent of calorimeter or heat capacity of the calorimeter is defined as the mass of water which will be heated through 1°C by the same amount of heat required to rise the temperature of the body through 1°C .

$$Q = ms\Theta$$

Where, Q= quantity of the heat gain or lose by the substance

S= specific heat of the substance

Θ = temperature difference

'ms' (=W) is the water equivalent of the calorimeter.

Measurement of W (i.e, water equivalent of the calorimeter) is necessary because during the heat exchange, the calorimeter also takes some amount of heat evolved (due to the reaction) and hence should be taken into account.

Procedure:

a) Determination of the water equivalent of the calorimeter:

50ml of distilled water was taken by measuring cylinder in the inner beaker of the calorimeter at laboratory temperature. A thermometer was adjusted to read the temperature of the distilled water for a period of 5 minutes at one minute interval (with 0.1°C accuracy). In another similar beaker, 50ml of hot water was taken (by measuring cylinder) and readings were recorded in the same way. [Note: i) The temperature of the hot water should be $10\text{-}15^{\circ}\text{C}$ higher than the laboratory temperature. ii) After measuring the temp of hot water, thermometer tip should be washed under tap water to bring the Hg level down). 50ml of this same hot water is then added in the distilled water kept in calorimeter and stirred well. The temperature of this water was noted at every one minute for five minutes.

Graph of temperature vs time was plotted. A vertical line was drawn on the graph for the moment of mixing when half of the water has been poured. On extrapolation of the temperature lines to this vertical line, the intersection points provide the temperatures of distilled water (t_1), hot water (t_2) and mixture (of distilled and hot water) (t_3). These were used for the calculation.

Observation and Calculation:

a) Determination of the water equivalent of the calorimeter

Vol. of RT water: 50ml

Vol. of hot water: 50ml

Room temp. water		Hot water		Mixture	
Time (min)	Temp ($^{\circ}\text{C}$)	Time (min)	Temp ($^{\circ}\text{C}$)	Time (min)	Temp ($^{\circ}\text{C}$)
1					
2					
3					

4					
5					

From graph(a):

Temp. of room temp. water: $t_1 = \dots\dots\dots^\circ\text{C}$

Temp. of hot water: $t_2 = \dots\dots\dots^\circ\text{C}$

Temp. of mixed water: $t_3 = \dots\dots\dots^\circ\text{C}$

Heat taken by calorimeter: $m_s (t_3 - t_1)$

Heat taken by room temp. water = $50 \times 1 \times (t_3 - t_1)$

Heat given by hot water = $50 \times 1 \times (t_2 - t_3)$

Heat taken = Heat given

$m_s (t_3 - t_1) + 50 \times 1 \times (t_3 - t_1) = 50 \times 1 \times (t_2 - t_3)$

$m_s = W = [50 \times 1 \times (t_1 + t_2 - 2t_3)] / (t_3 - t_1) \text{ cal}$

Hence, the water equivalent of calorimeter was $\dots\dots\dots\text{g}$

Theoretically, $W = \text{mass of beaker} \times \text{specific heat of glass} (\sim 0.2)$

Result: Water equivalent of the calorimeter was : $\dots\dots\dots\text{g}$

Experiment no. 7:

Objective: To determine the water equivalent of calorimeter and the heat of neutralization of strong acid (0.5N aq. HCl solution) and strong base (0.5N aq. NaOH solution).

Theory: The water equivalent of calorimeter or heat capacity of the calorimeter is defined as the mass of water which will be heated through 1°C by the same amount of heat required to rise the temperature of the body through 1°C.

$$Q = ms\Theta$$

Where, Q= quantity of the heat gain or lose by the substance

S= specific heat of the substance

Θ= temperature difference

'ms' (=W) is the water equivalent of the calorimeter.

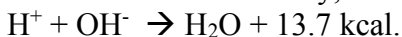
Measurement of W (i.e, water equivalent of the calorimeter) is necessary because during the heat exchange, the calorimeter also takes some amount of heat evolved (due to the reaction) and hence should be taken into account.

Heat of neutralization is the quantity of the heat evolved when one gram equivalent of an acid is neutralized by one gram-equivalent of a base or vice-versa in dilute solution at constant surrounding temperature. When both acid and base are strong, the heat released is maximum and is 13.7 kcal.

In case of aq. HCl and aq. NaOH, the following reaction takes place:



As both acid and base are strong, they remain 100% dissociated in solution and the the above reaction is actually,



Hence, in other way, heat of neutralization is the amount of heat released when a mole of water produced from complete reaction of an acid and base. If acid or base is a weak electrolyte, heat evolved (i.e., heat of neutralization) will be less.

Procedure: Determination of the heat of neutralization involves the following two steps:

b) Determination of the water equivalent of the calorimeter:

50ml of distilled water was taken by measuring cylinder in the inner beaker of the calorimeter at laboratory temperature. A thermometer was adjusted to read the temperature of the distilled water for a period of 5 minutes at one minute interval (with 0.1°C accuracy). In another similar beaker, 50ml of hot water was taken (by measuring cylinder) and readings were recorded in the same way. [Note: i) The temperature of the hot water should be 10-15°C higher than the laboratory temperature. ii) After measuring the temp of hot water, thermometer tip should be washed under tap water to bring the Hg level down). 50ml of this same hot water is then added in the distilled water kept in

calorimeter and stirred well. The temperature of this water was noted at every one minute for five minutes.

b) Determination of the heat of neutralization: The water was removed completely from the inner beaker of the calorimeter and 50ml of 0.5N NaOH solution was taken by the measuring cylinder at the RT. Thermometer was placed in the NaOH solution and the temperatures were recorded for 5 mins at the interval of one minute. 0.5N HCl solution was similarly taken in another beaker and temperatures were recorded. The same HCl solution was then added gently in the NaOH solution (which was kept in the inner beaker of the calorimeter. Note: care should be taken not to splash the solution). Temperatures were recorded for 5 min at one min interval.

Graph of temperature vs time was plotted. A vertical line was drawn on the graph for the moment of mixing when half of the water has been poured. On extrapolation of the temperature lines to this vertical line, the intersection points provide the temperatures of distilled water (t_1), hot water (t_2) and mixture (of distilled and hot water) (t_3). These were used for the calculation.

Similarly, a graph was drawn for heat of neutralization and temp of NaOH solution (t_4), HCl solution (t_5) and reaction mixture (t_6) were obtained.

Observation and Calculation:

b) Determination of the water equivalent of the calorimeter

Vol. of RT water: 50ml

Vol. of hot water: 50ml

Room temp. water		Hot water		Mixture	
Time (min)	Temp ($^{\circ}$ C)	Time (min)	Temp ($^{\circ}$ C)	Time (min)	Temp ($^{\circ}$ C)
1					
2					
3					
4					
5					

From graph(a):

Temp. of room temp. water: $t_1 = \dots\dots^{\circ}$ C

Temp. of hot water: $t_2 = \dots\dots^{\circ}$ C

Temp. of mixed water: $t_3 = \dots\dots^{\circ}$ C

Heat taken by calorimeter: $m_s (t_3 - t_1)$

Heat taken by room temp. water = $50 \times 1 \times (t_3 - t_1)$

Heat given by hot water = $50 \times 1 \times (t_2 - t_3)$

Heat taken = Heat given

$m_s (t_3 - t_1) + 50 \times 1 \times (t_3 - t_1) = 50 \times 1 \times (t_2 - t_3)$

$m_s = W = [50 \times 1 \times (t_1 + t_2 - 2t_3)] / (t_3 - t_1)$ cal

Hence, the water equivalent of calorimeter was $\dots\dots$ g

Theoretically, $W = \text{mass of beaker} \times \text{specific heat of glass} (\sim 0.2)$

c) Determination of the heat of neutralization:

Vol. of N/2 NaOH solution: 50ml

Vol. of N/2 HCl solution: 50ml

N/2 NaOH solution		N/2 HCl solution		Reaction mixture	
Time (min)	Temp ($^{\circ}\text{C}$)	Time (min)	Temp ($^{\circ}\text{C}$)	Time (min)	Temp ($^{\circ}\text{C}$)
1		6		12	
2		7		13	
3		8		14	
4		9		15	
5		10		16	

From graph (b):

Temp. of N/2 NaOH solution: $t_4 = \dots\dots^{\circ}\text{C}$

Temp. of N/2 HCl solution: $t_5 = \dots\dots^{\circ}\text{C}$

Temp. of reaction mixture: $t_6 = \dots\dots^{\circ}\text{C}$

Heat evolved in the reaction of 50ml N/2 NaOH solution with 50ml N/2 HCl solution:

$$= (100 + W) \times s \times \{t_6 - (t_4 + t_5)/2\} \text{ cal}$$

$$= (100 + W) \times s \times \{t_6 - (t_4 + t_5)/2\} \times 40 \text{ cal/g-equivalent}$$

$$= [(100 + W) \times s \times \{t_6 - (t_4 + t_5)/2\}] / 1000 \text{ kcal/g-equivalent}$$

$$\cong 13.7 \text{ kcal/g-equivalent}$$

[It is multiplied by 40 because we need to find the heat evolved for reaction involving 1000ml 1N acid or base (which contains 1 g-equivalent of acid or base). Hence to transfer 50ml N/2 to 1000ml 1N, we have to multiply by 40]

Result: Water equivalent of the calorimeter was : $\dots\dots$ g

Heat of neutralization of the strong acid and strong base reaction was $\dots\dots\dots$ kcal/g-equivalent

Experiment no. 8:

Objective: To determine the heat of neutralization of a weak acid (aq. acetic acid solution) by a strong base (aq. NaOH solution).

Theory: The heat of dissociation of a weak acid or a weak base may be defined as the change in enthalpy of the system when one gram equivalent of a substance is dissociated into corresponding ions.

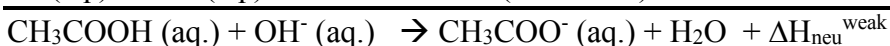
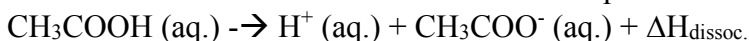
The neutralization of a strong acid with a strong base may be represented as:



If however, the acid or alkali is weak, enthalpy of neutralization is different because the reaction then involves the dissociation of weak acid /alkali as well. Hence, neutralization of a weak acid/base takes place in two steps:

- i) dissociation of weak acid/base
- ii) combination of $\text{H}^+ (\text{aq.})$ and $\text{OH}^- (\text{aq.})$ to form H_2O

The neutralization of acetic acid can thus be represented as:



[Note that the heat of neutralization for a strong acid and strong base is constant and is 13.7kcal/g-equiv but heat of neutralization for an weak acid/base must be less than 13.7kcal/g-equ. The heat of neutralization of reaction is –ve (exothermic).]

Procedure: (same as last experiment)

- a) Determination of the water equivalent of the calorimeter:
- b) Determination of the heat of neutralization:

Observation and Calculation:

- a) Determination of the water equivalent of the calorimeter

Vol. of RT water: 50ml

Vol. of hot water: 50ml

Room temp. water		Hot water		Mixture	
Time (min)	Temp ($^{\circ}\text{C}$)	Time (min)	Temp ($^{\circ}\text{C}$)	Time (min)	Temp ($^{\circ}\text{C}$)
1					
2					
3					
4					
5					

From graph(a):

Temp. of room temp. water: $t_1 = \dots\dots\dots^{\circ}\text{C}$

Temp. of hot water: $t_2 = \dots\dots\dots^{\circ}\text{C}$

Temp. of mixed water: $t_3 = \dots\dots\dots^{\circ}\text{C}$

Heat taken by calorimeter: $m_s (t_3 - t_1)$

Heat taken by room temp. water= $50 \times 1 \times (t_3 - t_1)$
 Heat given by hot water= $50 \times 1 \times (t_2 - t_3)$
 Heat taken = Heat given
 $m_s (t_3 - t_1) + 50 \times 1 \times (t_3 - t_1) = 50 \times 1 \times (t_2 - t_3)$
 $m_s = W = [50 \times 1 \times (t_1 + t_2 - 2t_3)] / (t_3 - t_1)$ cal
 Hence, the water equivalent of calorimeter wasg

b) Determination of the heat of neutralization for weak acid:

Vol. of N/2 NaOH solution: 50ml
 Vol. of N/2 acetic acid solution: 50ml

N/2 NaOH solution		N/2 HCl solution		Reaction mixture	
Time (min)	Temp ($^{\circ}$ C)	Time (min)	Temp ($^{\circ}$ C)	Time (min)	Temp ($^{\circ}$ C)
1		6		12	
2		7		13	
3		8		14	
4		9		15	
5		10		16	

From graph (b):
 Temp. of N/2 NaOH solution: $t_4 = \dots\dots^{\circ}$ C
 Temp. of N/2 HCl solution: $t_5 = \dots\dots^{\circ}$ C
 Temp. of reaction mixture: $t_6 = \dots\dots^{\circ}$ C

Heat evolved in the reaction of 50ml N/2 acetic acid solution with 50ml N/2 NaOH solution:

$$= (100 + W) \times s \times \{t_6 - (t_4 + t_5) / 2\} \text{ cal}$$

$$= (100 + W) \times s \times \{t_6 - (t_4 + t_5) / 2\} \times 40 \text{ cal/g-equivalent}$$

$$= [(100 + W) \times s \times \{t_6 - (t_4 + t_5) / 2\}] / 1000 \text{ kcal/g-equivalent}$$

$$\Delta H_{\text{neutral}}^{\text{Weak}} \approx \dots\dots (< 13.7 \text{ kcal/g-equivalent})$$

[It is multiplied by 40 because we need to find the heat evolved for reaction involving 1000ml 1N acid or base (which contains 1 g-equivalent of acid or base). Hence to transfer 50ml N/2 to 1000ml 1N, we have to multiply by 40]

Result: Water equivalent of the calorimeter was : g
 Heat of neutralization of acetic acid by a strong base was found to be.....kcal/g-equivalent

Experiment no. 9:

Objective: To determine the heat of dissociation of a weak acid (aq. acetic acid solution) by a strong base (aq. NaOH solution).

Theory: The heat of dissociation of a weak acid or a weak base may be defined as the change in enthalpy of the system when one gram equivalent of a substance is dissociated into corresponding ions.

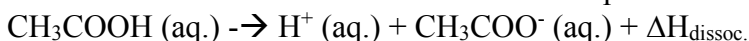
The neutralization of a strong acid with a strong base may be represented as:



If however, the acid or alkali is weak, enthalpy of neutralization is different because the reaction then involves the dissociation of weak acid /alkali as well. Hence, neutralization of a weak acid/base takes place in two steps:

- iii) dissociation of weak acid/base
- iv) combination of H^+ (aq.) and OH^- (aq.) to form H_2O

The neutralization of acetic acid can thus be represented as:



[Note that the heat of neutralization for a strong acid and strong base is constant and is 13.7kcal/g-equiv but heat of neutralization for an weak acid/base must be less than 13.7kcal/g-eq. The heat of neutralization of reaction is -ve (exothermic) whereas heat of dissociation is +ve (endothermic).]

Procedure: (same as last experiment)

b) *Determination of the water equivalent of the calorimeter:*

b) Determination of the heat of neutralization:

Observation and Calculation:

c) Determination of the water equivalent of the calorimeter

Vol. of RT water: 50ml

Vol. of hot water: 50ml

Room temp. water		Hot water		Mixture	
Time (min)	Temp ($^{\circ}\text{C}$)	Time (min)	Temp ($^{\circ}\text{C}$)	Time (min)	Temp ($^{\circ}\text{C}$)
1					
2					
3					
4					
5					

From graph(a):

Temp. of room temp. water: $t_1 = \dots\dots^{\circ}\text{C}$

Temp. of hot water: $t_2 = \dots\dots^{\circ}\text{C}$

Temp. of mixed water: $t_3 = \dots\dots^\circ\text{C}$
 Heat taken by calorimeter: $m_s (t_3 - t_1)$
 Heat taken by room temp. water = $50 \times 1 \times (t_3 - t_1)$
 Heat given by hot water = $50 \times 1 \times (t_2 - t_3)$
 Heat taken = Heat given
 $m_s (t_3 - t_1) + 50 \times 1 \times (t_3 - t_1) = 50 \times 1 \times (t_2 - t_3)$
 $m_s = W = [50 \times 1 \times (t_1 + t_2 - 2t_3)] / (t_3 - t_1) \text{ cal}$
 Hence, the water equivalent of calorimeter was $\dots\dots\text{g}$

d) Determination of the heat of neutralization for weak acid:

Vol. of N/2 NaOH solution: 50ml
 Vol. of N/2 acetic acid solution: 50ml

N/2 NaOH solution		N/2 HCl solution		Reaction mixture	
Time (min)	Temp ($^\circ\text{C}$)	Time (min)	Temp ($^\circ\text{C}$)	Time (min)	Temp ($^\circ\text{C}$)
1		6		12	
2		7		13	
3		8		14	
4		9		15	
5		10		16	

From graph (b):

Temp. of N/2 NaOH solution: $t_4 = \dots\dots^\circ\text{C}$
 Temp. of N/2 HCl solution: $t_5 = \dots\dots^\circ\text{C}$
 Temp. of reaction mixture: $t_6 = \dots\dots^\circ\text{C}$

Heat evolved in the reaction of 50ml N/2 acetic acid solution with 50ml N/2 HCl solution:

$$= (100 + W) \times s \times \{t_6 - (t_4 + t_5)/2\} \text{ cal}$$

$$= (100 + W) \times s \times \{t_6 - (t_4 + t_5)/2\} \times 40 \text{ cal/g-equivalent}$$

$$= [(100 + W) \times s \times \{t_6 - (t_4 + t_5)/2\}] / 1000 \text{ kcal/g-equivalent}$$

$$\Delta H_{\text{neutra}}^{\text{Weak}} \cong \dots\dots (< 13.7 \text{ kcal/g-equivalent})$$

[It is multiplied by 40 because we need to find the heat evolved for reaction involving 1000ml 1N acid or base (which contains 1 g-equivalent of acid or base). Hence to transfer 50ml N/2 to 1000ml 1N, we have to multiply by 40]

Heat of dissociation, $\Delta H_{\text{dissoc}}^{\text{Weak}} = \Delta H_{\text{neutra}}^{\text{Weak}} - \Delta H_{\text{neutra}}^{\text{Strong}}$

[Note: Input the numerical values of $\Delta H_{\text{neutra}}^{\text{Strong}}$ and $\Delta H_{\text{neutra}}^{\text{Weak}}$ with negative sign since they represent exothermic processes]

Result: Water equivalent of the calorimeter was : $\dots\dots\text{g}$

Heat of dissociation of acetic acid and strong base reaction was found to be $\dots\dots\text{kcal/g-equivalent}$

Experiment no. 10:

To determine the basicity of the given acid (M/2) calorimetrically.

Theory: The basicity of an acid is defined as the number of replaceable hydrogen ions in that particular acid. It may be mono, di or tri basic. 50 ml of a M/2 acid, where basicity in “*n*” will neutralize $50 \times n$ ml of N/2 NaOH solution. This fact is utilized to find “*n*” (basicity) of an acid calorimetrically.

Case 1; if $n = 1$, then 50 ml of M/2 acid will neutralize 50 ml of N/2 NaOH. Let the heat of reaction per mole of acid be **Q₁**.

Case 2; if $n = 2$, then 33.3 ml of M/2 acid will neutralize 66.7 ml of N/2 NaOH. Let the heat of reaction per mole of acid be **Q₂**.

Case 3; if $n = 3$, then 25 ml of M/2 acid will neutralize 75 ml of N/2 NaOH and let the heat of reaction per mole of the acid be **Q₃**.

(Since 100 ml of water is used to get the water equivalent, total volume of acid and alkali was kept at 100 ml).

If, it is found that $Q_1 \cong Q_2 \cong Q_3$, then the acid is monobasic.

If, it is found that $Q_3 \cong Q_2 > Q_1$ then the acid is dibasic (Note: there may be a small difference between Q_2 and Q_3 due to dilution.).

If, the acid is tribasic, then $Q_3 > Q_2 \gg Q_1$.

[where, Q_1 is the heat evolved for the 1/3 neutralization

Q_2 is the heat evolved for the 2/3 neutralization

Q_3 is the heat evolved for the complete neutralization]

Procedure:

(a) *Determination of water equivalent:* As mentioned in previous experiments.

(b) *Determination of Q₁* : 50 ml of N/2 NaOH was taken in a calorimeter (whose water equivalent was determined) and temperature was noted in 4 minutes with 1 minute interval. Then temperature of 50 ml M/2 acid was noted following the same procedure. The same acid was then added gently to the NaOH solution and the temperature was noted down in 4 minutes at 1 minute interval. The heat evolved Q_1 was calculated by using the formula:

$$Q_1 = \frac{(100+w) \times [t_6 - (t_4 + t_5) / 2] \times 1000}{M/2 \times 50} \text{ cal/mol}$$

where, t_4 , t_5 and t_6 are the temperatures of 50ml N/2 NaOH, 50ml M/2 acid and their mixture respectively.

Similarly, Q_2 and Q_3 were determined.

Observation & Calculation:

(A) For water equivalent

(B) For Q₁ : Vol. of acid (M/2) = 50 ml
Vol. of NaOH (N/2) = 50 ml

Table: Variation of temperatures with time for different solutions.

Acid		NaOH		Mixture	
Time/min	Temp./°C	Time/min	Temp./°C	Time/min	Temp./°C

Determined from the graph:

t₄ = temp. of acid

t₅ = temp. of NaOH

t₆ = temp. of Acid-NaOH mixture

Heat evolved = Q₁ = = kcal/mol

(C) for Q₂ = (using 33.3 ml acid + 66.7 ml NaOH)

(D) for Q₃ = (using 25 ml acid + 75 ml NaOH)

(Note: change the volume of acid in the equation for Q₂ and Q₃ determination)

Results: The heat of reactions = Q₁ = kcal/mol
 Q₂ = kcal/mol
 Q₃ = kcal/mol

Since, Q₃ ... Q₂ Q₁ ; the acid is mono/di/tri basic (n = 1/2/3)