

Experiment

Determine the water-equivalent of a calorimeter.

Requirements

Calorimeter, thermometer, clamp stand, beaker, measuring cylinder, glass stirrer, hot water, room temperature (RT) water.

Principle: The water equivalent of a calorimeter is the mass of water that would absorb or release the same amount of heat as the calorimeter itself for a temperature change of 1°C. It is a quantity expressed in mass units (like grams) and represents the thermal capacity of the calorimeter in terms of water, allowing it to be included in heat calculations as if it were an equivalent mass of water.

 $O = ms\theta$

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 considered.

Procedure:

a) Determination of the water equivalent of the calorimeter:

- 1. 50ml of distilled water was taken by measuring cylinder in 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).
- 2. In another similar beaker, 50 ml 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 allow the temp to come to the room temp). 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.
- 3. A 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 had been poured. On extrapolation of the temperature lines to this vertical line, the intersection points provide the temperatures of distilled water (t₁), hot water (t₂) and mixture (of distilled and hot water) (t₃). These values 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 (⁰ C)	Time (min)	Temp (⁰ C)	Time (min)	Temp (⁰ C)
1					
2					
3					
4					
5					

From graph(a):

Temp. of room temp. water: $t_1 = \dots 0^{-1}$ C

Temp. of hot water: $t_2 = \dots {}^{0}C$ Temp. of mixed water: $t_3 = \dots {}^{0}C$

- Heat taken by calorimeter: $ms(t_3-t_1)$
- 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
- ms $(t_3-t_1) + 50 \times 1 \times (t_3-t_1) = 50 \times 1 \times (t_2-t_3)$
- ms=W= $[50 \times 1 \times (t_1+t_2-2t_3)]/(t_3-t_1)$

Hence, the water equivalent of calorimeter isg

[Theoretically, W= mass of beaker x specific heat of glass (\sim 0.2)]

Result: Water equivalent of the calorimeter was found to be $\ldots\ldots\, g$

Experiment

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

Requirements

Calorimeter, thermometer, clamp stand, beaker, measuring cylinder, glass stirrer, hot water, room temperature (RT) water, N/2 aq. acetic acid solution, N/2 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:

$$H^{+}(aq.) + OH^{-}(aq.) \rightarrow H_{2}O + \Delta H_{neu} (-13.7 \text{ kcal}).$$

If 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 H⁺ (aq.) and OH⁻ (aq.) to from H₂O

The neutralization of acetic acid can thus be represented as:

CH₃COOH (aq.) + H⁺ (aq.) + CH₃COO⁻ (aq.) +
$$\Delta$$
H_{dissoc.} H⁺ (aq.) + OH⁻ (aq.) \rightarrow H₂O + Δ H_{neu} (-13.7 kcal).

$$CH_{3}COOH~(aq.) + OH^{\text{-}}~(aq.)~~ \\ \boldsymbol{\rightarrow}~ CH_{3}COO^{\text{-}}~(aq.) + H_{2}O + \Delta H_{neu}{}^{weak}$$

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

Procedure:

- 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 (⁰ C)	Time (min)	Temp (⁰ C)	Time (min)	Temp (⁰ C)

1			
2			
3			
4			
5			

From graph(a):

Temp. of room temp. water: $t_1 = \dots ^0 C$

Temp. of hot water: $t_2 = \dots {}^{0}C$ Temp. of mixed water: $t_3 = \dots {}^{0}C$

- Heat taken by calorimeter: $ms(t_3-t_1)$
- 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
- ms $(t_3-t_1) + 50 \times 1 \times (t_3-t_1) = 50 \times 1 \times (t_2-t_3)$
- ms=W= $[50 \times 1 \times (t_1+t_2-2t_3)]/(t_3-t_1)$

Hence, the water equivalent of calorimeter isg

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 (⁰ C)	Time (min) Temp (⁰ C)		Time (min)	Temp (⁰ 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 = 0 C Temp. of N/2 HCl solution: t_5 = 0 C Temp. of reaction mixture: t_6 = 0 C

Heat evolved in the reaction of 50ml N/2 acetic acid solution with 50ml N/2 NaOH solution: Assuming density and specific heat of the solution to be same as that of water

=
$$(100 + W) x \{t_6 - (t_4 + t_5)/2\}$$
 cal
= $(100 + W) x \{t_6 - (t_4 + t_5)/2\}x$ 40 cal/g-equivalent
= $[(100 + W) x \{t_6 - (t_4 + t_5)/2\}]/1000$ kcal/g-equivalent

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

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

Result: Water equivalent of the calorimeter was found to be g

Heat of neutralization of acetic acid by a strong base was found to be (-) kcal/g-equivalent (exothermic)

Experiment

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

Requirements

Calorimeter, thermometer, clamp stand, beaker, measuring cylinder, glass stirrer, hot water, room temperature (RT) water, N/2 aq. acetic acid solution, N/2 NaOH Solution, N/2 aq. HCl 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:

$$H^{+}$$
 (aq.) + OH^{-} (aq.) $\rightarrow H_{2}O + \Delta H_{neu}$ (-13.7 kcal).

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 from H₂O

The neutralization of acetic acid can thus be represented as:

CH₃COOH (aq.)
$$\rightarrow$$
 H⁺ (aq.) + CH₃COO⁻ (aq.) + Δ H_{dissoc.} H⁺ (aq.) + OH⁻ (aq.) \rightarrow H₂O + Δ H_{neu} (-13.7 kcal).

CH₃COOH (aq.) + OH⁻ (aq.)
$$\rightarrow$$
 CH₃COO⁻ (aq.) + H₂O + Δ H_{neu}^{weak}

[Note that the heat of neutralization for a strong acid and strong base is constant and is 13.7kcal/g-eqiv but heat of neutralization for a weak acid/base must be less than

13.7kcal/g-equ. The heat of neutralization of reaction is –ve (exothermic) whereas heat of dissociation is +ve (endothermic).]

Procedure:

- 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 (⁰ C)	Time (min)	Temp (⁰ C)	Time (min)	Temp (⁰ C)
1					
2					
3					
4					
5					

From graph(a):

Temp. of room temp. water: $t_1 = \dots {}^{0}C$

Temp. of hot water: $t_2 = \dots {}^{0}C$ Temp. of mixed water: $t_3 = \dots {}^{0}C$

- Heat taken by calorimeter: $ms(t_3-t_1)$
- 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
- ms $(t_3-t_1) + 50 \times 1 \times (t_3-t_1) = 50 \times 1 \times (t_2-t_3)$
- ms=W= $[50 \times 1 \times (t_1+t_2-2t_3)]/(t_3-t_1)$

Hence, the water equivalent of calorimeter isg

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 solut	ion	Mixture of Na	OH and HCl
Time (min)	Temp (⁰ C)	Time (min) Temp (⁰ C)		Time (min)	Temp (⁰ 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 = 0 C Temp. of N/2 HCl solution: t_5 = 0 C Temp. of reaction mixture: t_6 = 0 C

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

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

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

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

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

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

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

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

Result: Water equivalent of the calorimeter was found to be: g Heat of dissociation or enthalpy of dissociation of acetic acid was found to be (+)......kcal/g-equivalent (endothermic)

Experiment

Determine the heat of solution of a given salt in water by calorimetric method.

Molecular weight of NH₄Cl is 53.49 g/mol Molecular weight of *anhydrous* CaCl₂ 111 g/mol

Requirements

Calorimeter, thermometer, clamp stand, beaker, measuring cylinder, glass stirrer, hot water, room temperature (RT) water, NH₄Cl, CaCl₂, weighing balance.

Theory:

The heat of solution (or enthalpy of solution) is the change in enthalpy, or heat, that occurs when one mole of a solute dissolves completely in a specified amount of solvent at constant pressure. It can be either endothermic (absorbing heat, causing the solution to cool), for example, in the case of NH₄Cl, or exothermic (releasing heat, causing the solution to warm), for example, in the case of CaCl₂, and is measured in units like kCal/mol or kJ/mol. This process involves breaking solute-solute and solvent-solvent bonds (endothermic) and forming new solute-solvent bonds (exothermic).

The heat of solution is determined by dissolving a small known amount of the salt in a given amount of solvent taken in a calorimeter. The rise / fall in temperature is determined (Δt) . The heat of solution can be calculated by the following formula:

$$\Delta H_{soln} = \frac{(m_{solvent} + W + m_{solute}) \times \Delta t \times M}{m_{solute}} \ cal/mol$$

$$\Delta H_{soln} = \frac{(m_{solvent} + w + m_{solute}) \times \Delta t \times M}{m_{solute}} \times \frac{1}{1000} \ kcal/mol$$

Where $m_{solvent}$ is mass of solvent (water), W is the water equivalent of calorimeter, s is the specific heat of the solution (approximated to be equal to 1) and Δt is the difference in temperature of solution and solvent at the time of mixing (fall / rise in temperature).

Note: The heat of solution is often defined at infinite dilution, which means the amount of solvent is in excess, such that adding more solvent does not change the enthalpy of solution.

Procedure:

- a) Determination of the water equivalent of the calorimeter:
- c) Determination of the heat of solution:

Observation and Calculation:

b) Determination of the water equivalent of the calorimeter

Vol. of RT water: 50 ml Vol. of hot water: 50 ml

Room temp. water		Hot water		Mixture	
Time (min)	Temp (⁰ C)	Time (min)	Temp (⁰ C)	Time (min)	Temp (⁰ C)
1					
2					
3					
4					
5					

From graph(a):

Temp. of room temp. water: $t_1 = \dots 0$ C

Temp. of hot water: $t_2 = \dots 0^0$ C

Temp. of mixed water: $t_3 = \dots 0$ C

Heat taken by calorimeter: ms (t_3-t_1)

Heat taken by RT 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

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

$$ms=W=[50 x 1 x (t_1+t_2-2t_3)]/(t_3-t_1) g$$

Hence, the water equivalent of calorimeter isg

d) Determination of the heat of solution:

Vol. of RT water: 100 ml

Amount of salt (mention name of salt NH₄Cl): 3.0 g and 6.0 g

RT water, 100 ml		Solution of 3. salt	0 g NH ₄ Cl	Solution of 6.0 g NH ₄ Cl salt	
Time (min)	Temp (⁰ C)	Time (min) Temp (⁰ C)		Time (min)	Temp (⁰ C)
1		6		11	
2		7		12	
3		8		13	
4		9		14	
5		10		15	

From graph (b):

Temp. of RT water: $t_4 = \dots ^0 C$

Temp. of salt solution with 3.0 g of salt: t_5 = 0 C Temp. of salt solution with 6.0 g of salt: t_6 = 0 C

Amount of heat absorbed in the dissolution of 100 ml RT water and 3.0 g NH₄Cl

$$q_1 = (100 + W + 3.0) \times (t_5 - t_4) \ cal = \frac{(100 + W + 3.0) \times (t_5 - t_4)}{1000} kcal$$

So,
$$\Delta H_{solution1} = \frac{(100+W+3.0)\times(t_5-t_4)}{1000} \times \frac{53.49}{3.0} \ kcal/mol$$

Amount of heat absorbed in the dissolution of 100 ml RT water and 6.0 g NH₄Cl

$$q_2 = (100 + W + 6.0) \times (t_6 - t_4) \ cal = \frac{(100 + W + 6.0) \times (t_6 - t_4)}{1000} kcal$$

$$\Delta H_{solution2} = \frac{(100 + W + 6.0) \times (t_6 - t_4)}{1000} \times \frac{53.49}{6.0} \ kcal/mol$$

Result: Water equivalent of the calorimeter was found to be: g Heat of solution or enthalpy of solution of NH₄Cl was found to be (+)......kcal/mol (endothermic)

Heat of solution or enthalpy of solution of CaCl₂ was found to be (-)......kcal/mol (exothermic). {write like this if you do experiment with CaCl₂}

The amount of heat absorbed or evolved (q_1 and q_2) are different for different amounts of salt. But molar enthalpy of solution ($\Delta H_{solution}$) from both measurements show similar values. Small variations can happen due to experimental/measurement errors.