**Calorimetry**

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**Aim:**

1. To determine calorimeter constant.

2. To determine molar enthalpy change of solution.(NaCl,KCl,NH4Cl)

**Apparatus:** Calorimeter, graduated cylinder, thermometer, stirring ring, Bunsen burner.

**Theory:**

Calorimetry is the science of measuring the quantities of heat released or absorbed during a chemical reaction. The amount of heat that flows in or out of system depends on (1)The quantity of matter,(2) The identity of matter,(3) The temperature change experienced by the system.

The Heat capacity C is a measure of how a substance responds to the absorption or release of heat; substances that have a low value of C Such as iron (C= 0.45 J/(g・°C)) tend to be good conductors of heat whereas substances that have a high value of C Such as water (C=4.18J/(g・°C)) tend to be good insulators Ideally, the calorimeter is a perfect insulator, that is, it should prevent the loss of heat from the system to the surroundings and it should not allow heat from the surroundings to enter the system. In practice, this state of affairs is extremely difficult to achieve: heat is inevitably ex-changed between the system and the surroundings.

When a quantity of hot water is poured into a quantity of cold water the following heat exchange takes place.





We employ following substitution:



Assuming density and heat capacity to be independent of temperature,



Plugging these equations in heat balance equation:



Density of water (Ρ):1 g/cc

Specific Heat of water (Cw): 4.18 J/g-°C

So,



*The molar enthalpy of reaction*:

At constant pressure the heat in or out of the system is equal to enthalpy change.

Suppose system consist of salt MB (s) that absorbs heat when dissolved in water in calorimeter.



Following heat exchange occurs,





ΔHsys on per mole basis,





Mass of salt solution,



ΔHsys on per mole basis



*Thermodynamics of solution:*

In principle a process of dissolving a salt MB(s) can be deconstructed into 3 steps.First, energy from surrounding must be invested to completely overcome the strong ion-ion intermolecular forces that are interacting the positive M+ ions to negative B- ions:



This quantity of energy is called lattice energy.

Next, the M+(g) ions are surrounded by water molecules and enter solution:



This quantity of energy is called enthalpy of solution of M+ ion

Finally, the B-(g) ions are surrounded by water molecules and enter solution:



This quantity of energy is called enthalpy of solution of B- ion.





ΔHsoln>0: Temperature of solution falls.

ΔHsoln<0: Temperature of solution rises.

***Calorimeter:***



**Procedure:**

*Determination of Calorimeter constant*

1. Use aluminium vessel as calorimeter. The solutions to be studied should be placed in insulated inner cup of calorimeter.

2. Measure 50mL of water using graduated cylinder. This volume corresponds to Vcw .Record it.

3. Pour water into inner cup of calorimeter. Replace the lid and record the temperature of water at 30sec interval till it stabilizes. The temperature at which it stabilizes is the initial temperature of cold water Tcwi.

4.Using a Bunsen burner, bring about 125 mL of deionised water to full boil in a beaker.Assume initial temperature of boiling water to be100°C.(Thwi).

5.Pour boiling water into calorimeter,replace the lid and vigorously agitate the contents of calorimeter by moving the stirring ring up and down.

6.Record the temperature 30sec after hot water is added to the calorimeter and at 30sec intervals thereafter for atleast 5min.Agitate the contents of the calorimeter throughout the data acquisition period.

7.At the end of data acquisition period, measure the total volume in calorimeter.Vtot

8.Volume of hot water, Vhw=Vtot-Vcw

*Determination of ΔH for NaCl,KCl,NH4Cl:*

1. Weigh 3-4 gm of NaCl.(low Concentration Run)

2. Measure 100mL of deionized water and place it in calorimeter.

3. Replace the lid and record the temperature of water at 30sec interval till it stabilizes. The temperature at which it stabilizes is the initial temperature Tsolni.

4.Add NaCl and vigorously agitate the contents of calorimeter by moving the stirring ring up and down.

5..Record the temperature 30sec after NaCl is added to the calorimeter and at 30sec intervals thereafter.Agitate the contents of the calorimeter throughout the data acquisition period.

6.Repeat the process for high concentration run.(4-5gm NaCl).

7.Repeat the process for KCl,NH4Cl.

**Observation Tables:**

A.Tabulate time-temperature data :

1. For Calorimeter constant calculation
2. For ΔH (NaCl,KCl,NH4Cl)

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| B.Observation Table (For Calorimeter constant calculation) | | | | | | | | | | | | | | |  |
| Vhw(mL) | | Vcw(mL) | | Thw,i(°C) | | Tcw,i(°C) | | Tmix(°C) | | Tmix-100 (°C) | Tmix(°C)-Tcw,i(°C) | | | |  |
|  |
|  | |  | | 100 | |  | |  | |  |  | | | |  |
|  | |  | |  | |  | |  | |  |  | |  | |  |
| C.Observation table for ΔH (NaCl,KCl,NH4Cl) | | | | | | | | | | | | | | |  |
| Run | m sys (g) | | Vsoln (mL) | | Tsoln,i(°C) | | Tmix(°C) | | ΔT=Tmix(°C)-Tsoln,i(°C) | | | Ccal (Calorimeter Constant) | | ΔH(kJ/mol) |  |
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|  |
| 1 |  | |  | |  | |  | |  | | |  | |  |  |
| 2 |  | |  | |  | |  | |  | | |  | |  |  |
|  |  | |  | |  | |  | |  | | | Mean | |  |  |
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**Calculations:**

1.Plot Ccal data,plotting time on x axis and temperature along y axis.

2.The line intersects y axis at t=0,corresponds to Tmix.

3.



4. For ΔH,Tmix obtained in the similar way.





**Precautions:**

1.Do not boil the water too far ahead of time.

2. If you add significantly less than 100mL of boiling water you will arrive at a value of Ccal that is negative, which is impossible.

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