Department: Chemistry Dept.

College: Education College

University: Salahaddin University

Subject: Thermodynamic Chemistry (practical)

Course Book: *Stage* 2**; First semester**

Lecturer's name: Lecturer Dr. Khozan A. Haji

Academic Year: 2022/2023

Course Book

1. Course name	Thermodynamics
2. Lecturer in charge	Dr.Khozan A. Haji
3. Department/ College	Chemistry/ Education
4. Contact	e-mail:khozan.haji@su.edu.krd
5. Time (in hours) per week	Practical: 3
6. Office hours	Thursday 10.5am – 12.5 pm or by appointment
7. Course code	
8. Teacher's academic profile	I graduated from the College of Education, Department of Chemistry in 1997 and got a bachelor's degree BSc in chemistry. After that. I then started to study MSc/Analytical Chemistry in 1998 at Salahaddin University. After finishing my MSc study in 2000, I worked in Collage of Education / Chemistry department, as an assistant lecturer. The teaching experience is practical in the analytical Physical, Industrial &Organic Chemistry. Finally, I received my PhD-Physical Chemistry in the same University in 2015. My academic and research program interest focus on Kinetic study; I have more than 4 published articles and going to publish some other articles.
9. Keywords	**Kinetic study, chalcones, spectrophotometry, bromination, rate of reaction.**

10. Course overview:

All matter exists in three states: gas, liquid and solid. A molecular level representation of gaseous, liquid and solid states. A gas consists of molecules separated wide apart in empty space. The molecules are free to move about throughout the container.

In this course we introduce the principles of chemical thermodynamics, in studying and evaluating the flow of energy into or out of a system, it will be useful to consider changes in certain properties of the system. These properties include temperature, pressure, volume and concentration of the system. Measuring the changes in these properties from the initial state to the final state, can provide information concerning changes in energy and related quantities such as heat and work.

11. Course objective:

It tells whether a particular physical or chemical change can occur under a given set of conditions of temperature, pressure and concentration. It also helps in predicting how far a physical or chemical change can proceed, until the equilibrium conditions are established.

12. Student's obligation

The student attendance in class two hours a week, preparation of the home works examinations and participate in the discussion in the classroom.

13. Forms of teaching

Different forms of teaching will be used to reach the objectives of the course: Direct

questions, Quizzes, Discussion and conclusions. Power point presentations

14. Assessment scheme

Exams: There will be 10 quiz and 10 report and 1 closed book exam given throughout the semester.

Each quiz carry out 1 degree, and any report 1.5 degree and exam 10 degree they considered = 35%.

Final Exam: The Final Exam is Comprehensive in all course outlines. Carry out 50% degrees of the grade.

Theoretical grade = 65%

Practical grade = 35%

15. Student learning outcome:

The student will learn the phase rules, chemical equilibrium, finding the equilibrium constant for different reactions, in addition to learning the colligative properties of a mixtures

16. Course Reading List and References:

1- P.Atkins, and J.DE Paula. " ATKINS Physical Chemistry "6th edition.

2- IRA N. Levine. "Physical Chemistry" 6th edition.

3- A. Bahl, B.S. Bahl, and G.D. Tuli " Essential of physical Chemistry" .

4- R.A. Alberty, and R.J. Silbey."Physical Chemistry" 2nd edition.

17. The Topics:	Lecturer's name
Experiment (1): Calculation of Heat of neutralization by calorimeter. In dilute solution strong acids and strong bases are completely dissociated to their ions. Furthermore, their salts are also completely dissociated in the solution. The neutralization of a strong acid by strong base may thus be written: $$H^+ + Cl^- + Na^+ + OH^- \longrightarrow NaCl + H_2O$$ $$H^+ + OH^- \longrightarrow H_2O$$	Dr.Khozan A. Haji **2 hours**
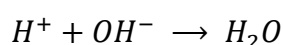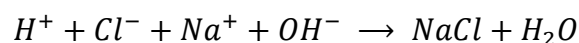
The heat effect is therefore independent of the nature of the anion of the acid and the cation of the base. The heat of neutralization may be determined by simple calorimeter.

Apparatus and chemicals:

Calorimeter, thermometer, stirrer, 0.1N KOH, 2N HCl

Procedure:

1- 100ml of 0.1N KOH is placed in a calorimeter, with continuous stirring record the temperature of the KOH solution every minute until 10min.

2- Add 16ml of 2N HCl to KOH solution and immediately record the temperature every minute until 10min.

Calculation:

1- Plot a graph between temp. ºC and time then find ΔT
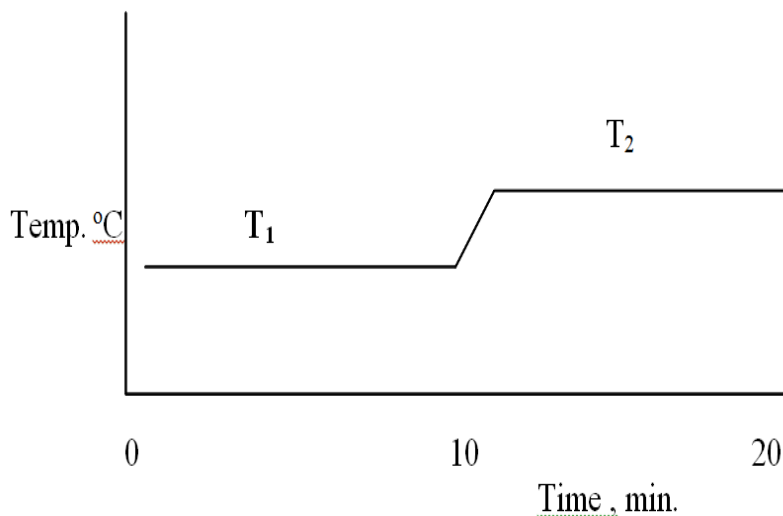
2- Calculate (q)

$$q = -(m_1 s_1 + m_2 s_2)\Delta T$$

m_1, m_2 = mass of calorimeter (with thermometer and stirrer) and

solution respectively.

s_1, s_2 =specific heat of calorimeter and solution respectively.

3- Find the amount (weight) of KOH present in 100ml of 0.1N, let this be x

4- Calculate ΔH.

$$\Delta H = \frac{q}{x} \times M.wt_{KOH}$$

Experiment (2): Calculation of Heat of solution.

Theory

The heat of solution is defined as : the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.

$$q = -(m_1 s_1 + m_2 s_2)\Delta T$$

Apparatus and chemicals:

Calorimeter, thermometer, stirrer, KNO_3.

Procedure:

1- 100ml of distilled water is placed in the calorimeter, with continuous stirring record the temperature of the water every minute until 10min.

2- Add 3.5g of KNO₃ to the water and immediately record the temperature, then take it every minute until 10min.

Calculation:

1- Plot a graph between temp. ᵒC and time then find ΔT
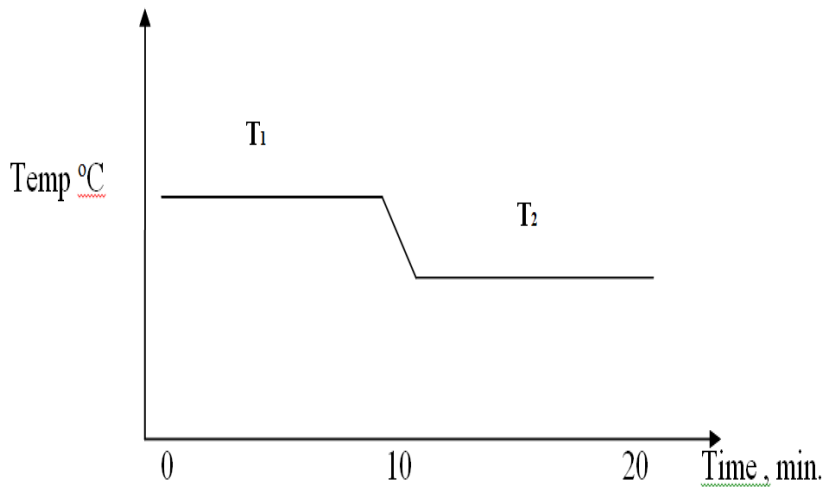
2- Calculate (q)

$$q = -(m_1 s_1 + m_2 s_2)\Delta T$$

3- Calculate ΔH.

$$\Delta H = \frac{q}{x} \times M.wt_{KNO_3}$$

Where x is the weight of KNO_3.

Experiment (3): Determination of Heat of solution from solubility.

Theory

The variation of the solubility of a substance with temperature is given by the relation:

$$\frac{d \ln S}{dT} = \frac{\Delta H_{sol.}}{RT^2} \dots\dots\dots\dots\dots (1)$$

Where S is the solubility of the substance and $\Delta H_{sol.}$ is the heat of solution. This relation ship may be regarded as a form of the van't Hoff isochore.

Assuming $\Delta H_{sol.}$ is constant between the temperature T_1 and T_2 and integrating equation (1) between these limits:

$$\ln \frac{S_1}{S_2} = \frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \dots \dots \dots \dots \dots (2)$$

Where S_1 is the solubility at the absolute temperature T_1, and S_2 is the solubility at the absolute temperature T_2.

If the solubility of a substance is determined at low different temperature; its heat of solution may be calculated by application of equation (2). If more accurate data are required solubility may be determined at several different temperature and ΔH may be obtained from a plot of lnS against $\frac{1}{T}$.

Apparatus and chemicals

Thermostats at 30, 40, 50, and 60 °C , benzoic acid potassium hydroxide (0.1N), pipette(25ml), phenolphthalein indicator, cotton wool .

Procedure

1- 250ml of KOH (0.1N) must be prepared.

2- 1gm of benzoic acid is placed in a beaker which contains 100ml of hot water at about 70ºC.

3- The beaker is placed in the thermostat at 60ºC and leaving it for 15min. for thermal equilibrium.

4- A small piece of rubber tubing containing a cotton wool is attached to a 25ml pipette and 10ml of solution is withdrawn. (Note: the pipette may be warred before use in order to prevent the crystallization of the solutions at the higher temperature)

5- Put 10ml of solution in a conical flask which contain 30ml of hot water, then by using phenolphthalein as an indicator, titrate the solution with (0.1N) KOH and record the volume of KOH
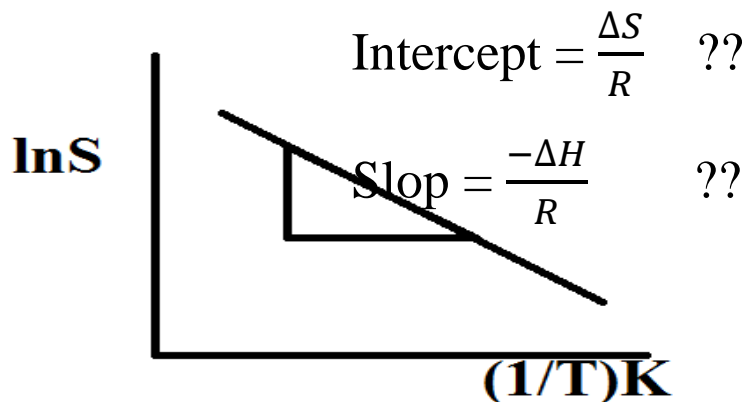
6- Repeat these procedures from (3-5) by changing the

temperature as (50,40 and 30°C).

Calculation

1- Calculate the concentration of benzoic acid at each temperature (S)

$$(N.V)_{KOH} = (N.V)_{Benzoic\ Acid} \quad \rightarrow \quad N_{B.A} = S$$

2- Draw the plot between $\ln S$ versus $\frac{1}{T}$.

$$\text{Intercept} = \frac{\Delta S}{R} \quad ??$$

$$\text{Slop} = \frac{-\Delta H}{R} \quad ??$$

ln S

(1/T)K

Experiment (4): Determining the enthalpy of combustion of an alcohol.

Heat of combustion is the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid H_2O if the compound contains C, H, and O.

Simple polystyrene calorimeter of low heat capacity can be used for any non–combustion reaction that will happen spontaneously at room temperature involving solutions or solid reacting/dissolving with/in a liquid like water and it doesn't matter if the reaction is exothermic or endothermic.

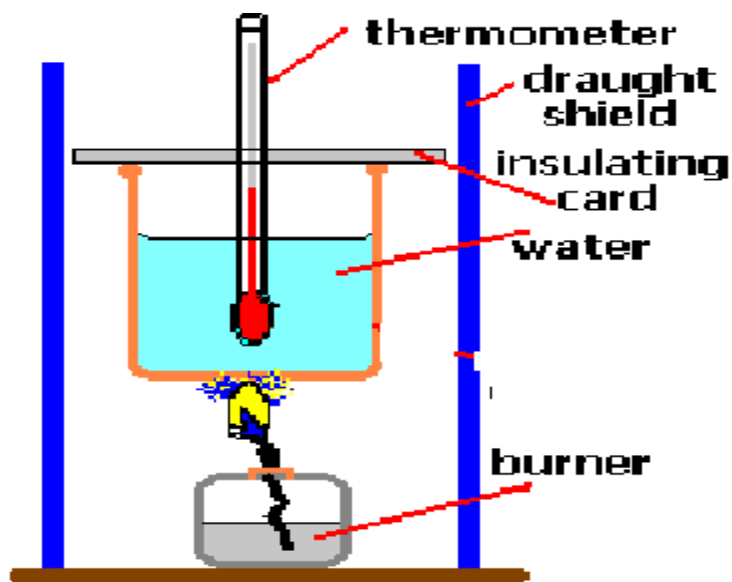A double polystyrene cup system provides good thermal insulation for the system.
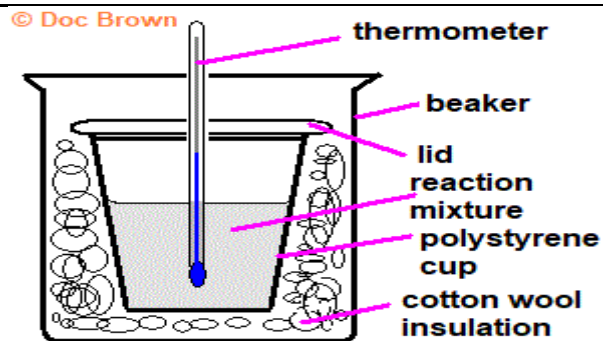
A simple well insulated calorimeter for measuring the thermal energy transfer in a chemical reaction

Apparatus and chemicals:

Beaker or Conical flask, Thermometer, Spirit burner.

Arrange the equipment as shown in the following figure:

Procedure:

3- Put 100 ml of water (100g) into the beaker (or conical flask).

4- The spirit burner contained the fuel ethanol CH_3CH_2OH and weighed 10g at the start.

5- Light the wick until the water temperature reaches ~70°C.

Calculation:

1- Calculate ΔT of water (before and after heating).

2- Calculate Δm of ethanol (before and after burning).

3- Calculate the enthalpy of combustion of ethanol.

$$Heat\ lost\ =\ -Heat\ gained$$

$$Q = m.S.\Delta T$$

$Q = Thermal\ energy\ (J)$

$m = mass\ of\ water$

$S = specific\ heat\ of\ water\ \left(1cal, or\ 4.18\ \frac{J}{g.^oC}\right)$

$\Delta T = temperature\ change\ of\ water$

$$\Delta H_c\ of\ ethanol = \frac{Q}{n}$$

$$n = mole\ of\ ethanol$$

Note:

We can calculate the heat of combustion or the efficiency of some other fuels.

https://www.youtube.com/watch?v=DWNsZfyFLr4

Experiment (5): Calculation of the heat capacity of different calorimeters.

Specific heat is defined by the amount of heat needed to raise the temperature of 1 gram of a substance 1 degree Celsius (°C). Water has a high specific heat capacity which we'll refer to as simply "heat capacity", meaning it takes more energy to increase the temperature of water compared to other substances. This is why water is valuable to industries and in your car's radiator as a coolant.

The Zeroth Law of Thermodynamics states: "If two samples of matter, initially at different temperatures (T_H and T_C, respectively), are placed in thermal contact, heat will be lost by the hotter sample (T_H) and gained by the cooler one (T_C). This exchange of heat will take place until both samples achieve the same final temperature, T_F.

Apparatus and chemicals:

Different calorimeter (Steel, Al, Cu, Glass)

Procedure:

1- Mix 100 gm of Hot water (about 65 °C) with 100g ordinary water (at lab. Temperature) into cup calorimeter.

2- Measure the temperature of the mixture about 5minutes.

3- Calculate the specific heat of the calorimeter.

4- Repeat these steps for other calorimeters.

Calculation:

$$Q_{ABS} = -Q_{REL}$$

$$Q_{hot\ water} = -(Q_{cold\ water} + Q_{calorimeter})$$

$$Q_{calorimeter} = -Q_{cold\ water} - Q_{hot\ water}$$

$$(C.\Delta T)_{calorimeter} = -(m.S.\Delta T)_{cold\ water} - (m.S.\Delta T)_{hot\ water}$$

$$\therefore\ C_{calorimeter} = \frac{-(m.S.\Delta T)_{cold\ water} - (m.S.\Delta T)_{hot\ water}}{\Delta T_{calorimeter}}$$

Note:

$$Specific\ heat\ capacity\ of\ calorimeter$$
$$= \frac{C_{calorimeter}}{mass\ of\ calorimeter}$$

$$C_{cal} = m_{cal} \times S_{cal}$$

How to Calculate a Calorimeter Constant?

Example 1: When 40.0 mL of water at 60.0 °C is added to 40.0 mL at 25.0 °C water already in a calorimeter, the temperature rises 15.0 °C. What is the calorimeter constant?

Solution:

1) Hot water lost:

$$Q = mS\Delta T = 40g \times 4.18\frac{J}{g.^{o}C} \times 20^{o}C = 3344$$

2) Cold water got:

$$Q = mS\Delta T = 40g \times 4.18\frac{J}{g.^{o}C} \times 15^{o}C = 2508J$$

3) The calorimeter got the rest:

$$3344 - 2508 = 836J$$

4) Find the heat capacity of the calorimeter:

$$C_{cal} = \frac{836J}{15^{o}C} = 55.73\ \frac{J}{^{o}C}$$

Experiment (6): Calculation of the specific heat of the substance.

The specific heat of the substance is the number of calories required to raise the temperature of one gram of the substance one degree centigrade.

The experimental determination of the specific heat of a metal by the method of mixtures consists in dropping a known mass of the metal at a known high temperature into a known mass of water at a known low temperature. The equilibrium temperature is then measured. The heat absorbed by the water, calorimeter, and stirrer is equal to the heat lost by the metal.

Apparatus and chemicals:

Cup calorimeter, different metal, oven.

Procedure:

1- Heat a metal (Known weight) to 100°C in oven.

2- Put the metal in a cup calorimeter which contained 100ml D.W.

3- Record the temperature before and after adding the metal

Calculation:

$$Q_{metal} = -(Q_{water} + Q_{cal})$$

Example: A piece of metal with a mass of 7.5g is heated to 200°C before being dropped into 100g of water. This causes water temperature to rise from 21.1°C to 30.8°C. What is the metals specific heat capacity?

Solution:

$$Q_{metal} = m.S.\Delta T$$

$$\therefore S_{metal} = \frac{Q_{metal}}{m_{metal} \times \Delta T}$$

$$-Q_{metal} = Q_{water}$$

$$Q_{water} = 100 \times 4.18 \times (30.8 - 21.1) = 4054.6\,J$$

$$\therefore S_{metal} = \frac{Q_{metal}}{m_{metal} \times \Delta T} = \frac{-4054.6}{7.5 \times (30.8 - 200)}$$

$$S_{metal} = 3.195\ \frac{J}{g.K}$$

Experiment (7): Determining the enthalpy of reaction of zinc displacing copper from copper (II) sulfate solution

Enthalpy is the amount of heat that is lost or gained by the atoms in a chemical reaction. Some reactions are endothermic and absorb heat from their surroundings. Some reactions are exothermic and lose heat to their surroundings.

When a more electropositive metal displaces a less electropositive metal from a solution of its salt, heat change occurs.

$$Zn + CuSO_4 \longrightarrow Cu + ZnSO_4$$
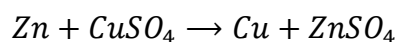
The literature value for this displacement reaction can be considered as -217kJ mol^{-1}.

Apparatus and chemicals:

Calorimeter, Zn powder, CuSO$_4$.

Procedure:

1- Pipette 50.0 ml 0.1 M copper (II) sulphate solution into a 100 ml expanded polystyrene cup. Record the temperature of the solution using a 0-50 °C thermometer.

2- Weigh 0.5 g zinc dust using a clean paper. Add the zinc dust to the copper(II) sulphate solution, at a time. Then, start the stop clock immediately.

3- Stir regularly with the thermometer. Record the temperature every minute for ten minutes.

Calculation:

$$Q_{reaction} = -(m \times S \times \Delta T)$$

$$Q_{reaction} = -(m \times 4.18 \times \Delta T)$$
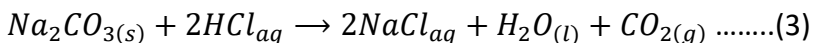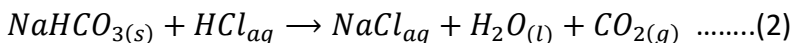
$$\Delta H_r = \frac{Q_{reaction}}{n}$$

$$n = minimum\ mole\ in\ the\ reaction$$

Experiment (8): Calculation the enthalpy of the decomposition of sodium hydrogen carbonates Using Hess's Law.

The enthalpy change of reaction for the decomposition of sodium hydrogen carbonate, $NaHCO_{3(s)}$, cannot be measured directly, then we must carry out two separate experiments and use the results of these experiments to determine the enthalpy change of reaction for the decomposition of sodium hydrogen carbonate.

$$2NaHCO_{3(s)} \longrightarrow Na_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \ ......(1)$$
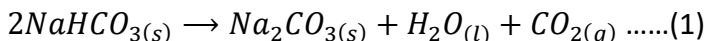
The two other reactions involve mixing sodium hydrogen carbonate and sodium carbonate with hydrochloric acid.

$$NaHCO_{3(s)} + HCl_{aq} \longrightarrow NaCl_{aq} + H_2O_{(l)} + CO_{2(g)} \ ....(2)$$

$$Na_2CO_{3(s)} + 2HCl_{aq} \longrightarrow 2NaCl_{aq} + H_2O_{(l)} + CO_{2(g)} \ ....(3)$$

$$\Delta H_{eq1} = 2 \times \Delta H_{eq2} - \Delta H_{eq3}$$

Apparatus and chemicals:

Calorimeter, $NaHCO_{3(s)}$, HCl, $Na_2CO_{3(s)}$.

Procedure:

1- Add 2g of $Na_2CO_{3(s)}$ to 50ml of 0.5M HCl, and then calculate ΔT.

2- Add 2g of $NaHCO_{3(s)}$ to 50ml of 0.5M HCl, and then calculate ΔT.

3- Calculate Q and then ΔH of each reaction.

4- Calculate ΔH of the decomposition of sodium hydrogen carbonates.

Experiment (9): Determination of Enthalpy of solution of Potassium dichromate by solubility.

Theory:

Potassium dichromate, $K_2Cr_2O_7$, is a common inorganic chemical reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications. As with all hexavalent chromium compounds. It is a crystalline ionic solid with a very bright, red-orange color.

Potassium dichromate has very small solubility at low temperature and does not contain crystal water. It is easily purified through recrystallization; also not easy to have deliquescence and thus often being used as the reference standard in the analysis.

Solubility in water: 4.9 g/100 ml at 0°C; 102 g/100 ml at 100 °C; insoluble in alcohol.

If the solubility of a potassium dichromate is determined at

different temperature; its heat of solution and entropy may be calculated by application of:

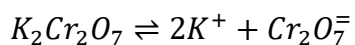$$\ln k = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Apparatus and chemicals

Thermostats, $K_2Cr_2O_7$.

Procedure

1- Dissolve five different amount of $K_2Cr_2O_7$ (1, 1.5, 2, 2.5, 3)g in 10ml of D.W. by increasing temperature.

2- Record the degree to which the salt dissolves, or when the first crystal appears when the solution is cooled.
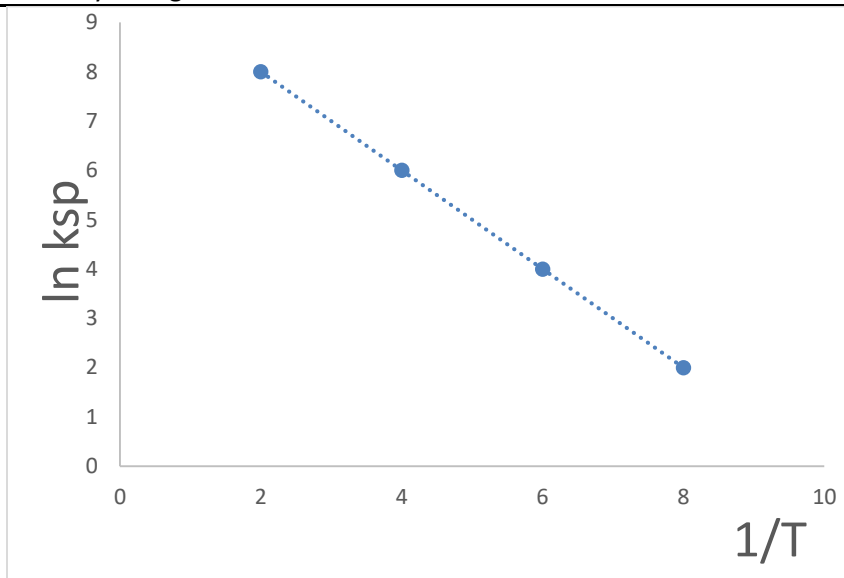
Calculation

1- Draw a plot between $\ln k_{sp}$ $verses$ $\frac{1}{T}$.

2- k_{sp} of $K_2Cr_2O_7$ can be calculated as follows:

$$K_2Cr_2O_7 \rightleftharpoons 2K^+ + Cr_2O_7^=$$

$$k_{sp(K_2Cr_2O_7)} = [2S]^2[S] = 4S^3$$

$$[S] = molarity\ of\ K_2Cr_2O_7$$

$$M_{K_2Cr_2O_7} = \frac{w \times 1000}{294 \times 10} \qquad w = (1, 1.5, 2, 2.5, 3)g$$

$$Intercept = \frac{\Delta S}{R}$$

$$Slope = \frac{-\Delta H}{R}$$

Experiment (10): Determination of Ethanol percentage by Heat of combustion.

In combustion reactions, some substances will release more energy than others.

Enthalpies of combustion can be used to compare which fuels or substances release the most energy when they are burned.

The heat of combustion of a substance, also known as the calorific value or the energy value, can be defined as the amount of heat liberated when a given amount of the substance undergoes combustion.

Typical combustion reactions involve the reaction of a carbon-containing material with oxygen to form carbon dioxide and

water as products. If methanol is burned in air, we have:

$$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$
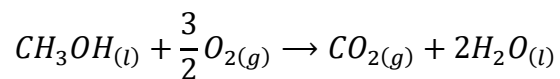
In this case, one and a half mole of oxygen reacts with one mole of methanol to form one mole of carbon dioxide and two moles of water.

We can use this simple model to estimate the heat of combustion of ethanol, and comparing the value of heat of combustion with others to find out the percentage of ethanol.
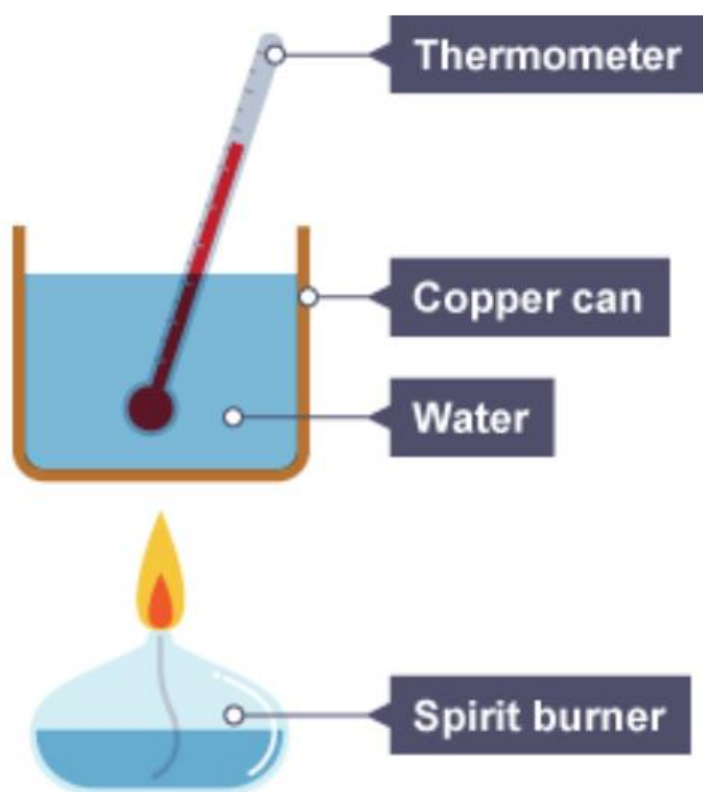
Apparatus and chemicals:

Beaker or Conical flask, Thermometer, Spirit burner.

Procedure:

6- Put 100 ml of water (100g) into the beaker (or conical flask).

7- The spirit burner contained the fuel ethanol CH₃CH₂OH and weighed 10g at the start.

8- Light the wick until the water temperature reaches ~70°C.

Calculation:

4- Calculate ΔT of water (before and after heating).

5- Calculate Δm of ethanol (before and after burning).

6- Calculate the enthalpy of combustion of ethanol.

$$Heat\ lost\ =\ -Heat\ gained$$

$$Q = m.S.\Delta T$$

$Q = Thermal\ energy\ (J)$

$m = mass\ of\ water$

$S = specific\ heat\ of\ water\ \left(1cal, or\ 4.18\ \frac{J}{g.^oC}\right)$

$\Delta T = temperature\ change\ of\ water$

$$\Delta H_c\ of\ ethanol = \frac{Q}{n}$$

$$n = mole\ of\ ethanol$$

4- Repeat the experiment for an unknown %ethanol, and calculate the percentage of ethanol in the sample.

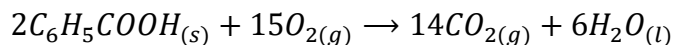How????

18. Exams

Q1: The calorific value of ethanol is $\left(-29.74\ \frac{kJ}{g}\right)$.Calculate the amount of ethanol required to heat 200ml of water from 25°C to 75°C.

(20M)

Q2: For the reaction
$$2C_6H_5COOH_{(s)} + 15O_{2(g)} \longrightarrow 14CO_{2(g)} + 6H_2O_{(l)}$$
$\Delta E = -772.7\ \frac{kJ}{mole}$.
Calculate ΔH_c for benzoic acid.

(20M)

Q3: Benzoic acid is slightly soluble salt in water, and its solubility is increased by increasing temperature. If 1g of benzoic acid dissolved in 100ml D.W. and this solution was heated to different temperatures, at every temperature 10ml of the solution titrated with standard NaOH solution (0.1N), the volume of standard NaOH changed with temperature as follows:

Volume of Benzoic acid solution/ml	10	10	10	10
Temperature/°C	30	40	50	60
Vol. of (0.1N) NaOH/ml	10	11.1	12.3	13.5

Calculate ΔS and ΔH of this process.

(20M)

Q4: Calculate the calorimeter constant if 25.0 g of water at 60.0 °C was added to 25.0 g of water at 25.0 °C with a resulting temperature of 35.0 °C?

(20M)

(20M)

Q5: If (C) change with (t) as follows:

C	0.49	0.47	0.46	0.45	0.43
t	20	60	80	100	150

Calculate C_o graphically if

$$lnC = lnC_o - kt$$

20. Extra notes:

21. Peer review