Exploring the Spontaneous Dissociation of Inorganic Salts: Thermodynamic Analysis and Reaction Kinetics in an Exothermic System

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Abstract. The current study was carried out to measure the heat resulting from the spontaneous dissociation of some inorganic salts by using sodium chlorate and ammonium perchlorate salts (3gm), iron filings (22gm) with grain size (350 µ), sawdust (7gm) with a size of (200 µ), activated carbon (7gm), and distilled water (8ml), The speed of the reaction was measured and found it was second degree (n=2). Measurement of the heat of the reaction emitted was also studied in several ways, including the direct method from the Vant-Hoff equation and the calorimetric method, in addition to comparing it with the theoretical value of standard heat of formation which showed the dependence of the reaction temperature on the two salts. Moreover, classical methods were used to determine the amount of chlorate and perchlorate radicals by depositional gravimetric analysis and volatilization methods.

Introduction

One of the main challenges at present is the protection of the environment, which is represented by the decreasing of the exhaustion of energy and natural pure materials and waste materials.
Management of waste and reusing by-products and research on recycling are significant issues worldwide [1]. Among the waste produced by construction and manufacturing operations are iron filings and sawdust.

Iron filings are generated as by-products of iron metal cutting, grinding, or milling of finished iron products [2]. When this waste is not properly recycled, it is discharged in large quantities into the environment, leading to the pollution of water bodies and blockage of drainage systems [3] Therefore, reusing this waste will be an alternative way to dispose of waste, while at the same time reducing problems attributed to pollution and disposal costs [4].

Sawdust is a waste from the wood, pulp, paper, and wood processing industries and is considered an industrial waste that pollutes the environment [5]. However, it can become a valuable commodity as an ore material in manufacturing, and building materials such as billboards, racks, house ceilings, and wall panels [6].

The sieving process is used to separate particles that are different in size, the fine particles can pass easily through holes while the large particles are disintegrated by colliding with each other [7].

Most hot packs work by dissolving salt in water, the salt disintegrates, and heat is emitted in an exothermic reaction, these packs often use calcium chloride or magnesium sulfate and rapid exothermic reactions cause many problems in selectivity and safety [8].

In previous studies, some researchers recommended the possibility of using aluminum, magnesium, and iron powder as fuel in ignition systems [9]. Aluminum and magnesium give higher temperatures than iron when they react with oxygen, but the period of maintaining the temperature is shorter, so iron filings are the ideal choice [10].

Current researches are focused on using phase-changing materials (PCM) such as some hydrides, salts, and inorganic complexes as well as some organic materials to use their ability to store thermal energy and exploit their exothermic interactions for domestic and commercial uses [11].

In this research, some chemical reactions were studied to use them in designing a thermochemical system, which includes an exothermic reaction that we benefit from in generating heat through studying the spontaneous dissociation of some inorganic salts which are of economic benefit in terms of their availability, and low economic costs.

Materials and Methods

Materials

-Iron filings which sieved on (350 µ).
- Sawdust that dried, grinded, and sieved on (200 µ).
- Ammonium perchlorate salt (NH_4ClO_4) with a concentration (95%)
- Sodium chlorate salt ($NaClO_3$) with a concentration (99%).
- Activated charcoal type (SP3-SG-103).

Methods

Temperature changes with changing components

several experiments were carried out by fixing the quantity or quality of one of the reactants and changing the others Thus, experiments continued to reach the ideal conditions (gradual increase in temperature) were obtained by using iron filings (22gm) with grain size of (350 µ), sawdust (7gm) with a size of (200 µ), sodium chlorate and ammonium perchlorate salts (3gm), activated carbon (7gm) and distilled water (8ml), the results show in tables (1,2,3,4,5).

Table 1. Changing the diameter of the iron filing with the temperature

diameter of iron filings grains (µ)	250	350	500	600	700
temperatures (C°)	55	55	33	31	28
time (m.)	10	20	15	30	20

Table 2. Changing the diameter of sawdust grains with temperature

diameter of sawdust particles (µ)	50	100	150	200	250
temperatures (C°)	29	33	32	55	47
time (m.)	50	25	25	20	20

Table 3. Changing the weight ratio for salts with temperature

weight of sodium chlorate and ammonium perchlorate/gm	1:1	2:2	3:3	4:4	5:5
temperatures (C°)	31	40	55	65	75
time (m.)	25	30	20	15	10

Table 4. Changing the volume of distilled water with temperature

volume of distilled water (ml.)	6	7	8	9	10
temperatures (C°)	31	41	55	47	42
time (m.)	15	30	20	25	20

Table 5. Changing the type of charcoal with the temperature

charcoal type	animal charcoal	activated charcoal
temperatures (C°)	44	55
time (m.)	25	20

Reaction kinetics

After determining the components and types of reactants in the mixture, the speed of the reaction was measured (change in concentration of the two salts, NH_4ClO_4 and $NaClO_3$ with time) by taking the remaining salts during the reaction after different periods (t.), measuring the amount of chlorate (ClO_3) by depending on classical methods such as depositional gravimetric analysis as well as analysis of the perchlorate ion (ClO_4) by the burning method, table 6 shows the components of the reaction mixture.

Table 6. Components of the reaction mixture

Material	Weight (gm)	No. of moles = $\dfrac{wt.(gm)}{m.wt}$
iron filings	22	0.3928
sawdust	7	
activated charcoal	7	
distilled water	8 ml	
sodium chlorate	3	0.02818 *
ammonium perchlorate	3	0.02553 **

*represents the initial concentration of the inorganic salt $NaClO_3$
**represents the initial concentration of the inorganic salt. NH_4ClO_4
By depending on the method of radical analysis for chlorate deposition obtained the results are shown in table 7.

Table 7. The deposition analysis for ClO^-_3

Time (min.)	$KClO_3$ weight (gm) *	$NaClO_3$ weight (gm) **	(a – x) *10^{-3} moles
0	0	0.06 $\neq$	28.18
10	0.0609	0.053	26.0
20	0.0552	0.048	25.0
30	0.0402	0.035	15.0
40	0.0287	0.025	8.5
50	0.0126	0.011	5.5
60	0.0086	0.0075	3.0

Measuring the heat of the reaction by Vant-Hoff equation

The temperature of the reaction was measured directly by applying Vant-Hoff equation, where the components of the mixture were mixed and the reaction rate constant (k) was calculated at room temperature (25°C) and calculated again at other temperatures. Thus, the rate of speed was measured several times, table 8 shows the change in chemical reaction rate with temperature.

Table 8. Changing of chemical reaction rate with temperature

experiment no.	T C $^\circ$	1/T (K^{-1})	k (min^{-1})	log K * 10^3
1	25	0.00329	0.0461	1.664
2	40	0.00315	0.056	1.748
3	56	0.00303	0.091	1.959
4	69	0.00292	0.191	2.28
5	74	0.00288	0.42	2.62
6	85	0.00279	0.63	2.799

Based on the results of table 8 and by applying the kinetic equations using the trial method, it was proven that the reaction is of the first order, table 9 shows the results.

Table 9. The reaction resulting from the kinetic equations is the first-order

Time (min.)	$\ln \dfrac{a}{a-x}$	k_1 (min^{-1})	$\dfrac{x}{a(a-x)}$	k_2 (mole^{-1} .min^{-1})
0	0	0	0	0
10	0.35	0.015	8.09	1.15
20	0.405	0.022	10.03	0.669
30	0.569	0.056	13.51	1.95
40	0.831	0.066	15.69	0.81
50	1.15	0.067	15.91	2.15
60	1.691	0.059	16.01	1.09

The perchlorate radical (ClO^-_4) in the ammonium perchlorate salt (NH_4ClO_4) was determined by deposition gravimetric analysis in the form of silver chloride using the volatility method, the results are shown in table 10.

Table 10. The deposition gravimetric analysis of ClO^-_4

Time (min)	AgCl weight (gm)	NH_4ClO_4 * weight (gm)	$(b-x)*10^{-3}$ moles
0	0	$\neq$ 0.072	25.53
10	0.079	0.065	23.0
20	0.07	0.05	15.0
30	0.065	0.035	7.0
40	0.05	0.025	5.3
50	0.042	0.011	3.0
60	0.032	0.007	1.5

$\neq$: represents the initial weight of the perchlorate radical in (1.2 gm) from relative calculations.

By applying the kinetic equations to deduce the reaction kinetics relative to the perchlorate radical or the ammonium perchlorate salt, appears the dependence of the reaction speed on the weights of salt, table 11 shows the results.

Table 11. The dependence of the reaction speed on the weights of ammonium perchlorate

Time (min)	$\ln \dfrac{b}{b-x}$	K_1 (min^{-1})	$\dfrac{x}{b(b-x)}$	K_2 (mole^{-1} . min^{-1})
0	0	0	0	0
10	0.26	0.041	6.91	0.81
20	0.315	0.046	8.61	1.5
30	0.591	0.061	10.9	0.51
40	0.75	0.05	13.5	0.81
50	1.05	0.04	35.6	0.69
60	1.43	0.039	45.6	0.78

From the mathematical application of the Vant-Hoff equation, can obtain an approximate value of the reaction temperature ($\Delta Hr = 2.382$ kcal/mole).

Measuring the heat of the reaction calorimetrically

Based on the equations for calculating the heat of the reaction calorimetrically, the calorimeter constant (C) must be calculated by using the special relationship between the total heat capacity (C) and the enthalpy of the reaction, the formulas for the Vant - Hoff equation can be used to calculate the enthalpy of the reaction as shown in table 12,13.

Table 12. Recorded temperatures versus time

Time (min.)	Temperature (C°)
0 – 3.5	32
3.5	35.5
4	35.1
4.5	34.7
5	34.3
5.5	33.9
6	33.5

Table 13. The relationship between volume and final solution titration and heat emitted

the volume of acid added	Final solution titration	The amount of heat emitted
3	1.1	0.945
2.5	0.918	0.784
2.3	0.842	0.718
1.5	0.552	0.473
0.75	0.227	0.242
0.6	0.217	0.191

From the mathematical application for the calorimeter constant can obtain an approximate value of the reaction temperature ($\Delta Hr = 1.643$ kcal/mole).

Measuring the heat of reaction theoretically

To calculate the heat of the reaction theoretically relied on the heat resulting from the dissociation of the two salts ($NaClO_3$ and NH_4ClO) according to the following equation:

$$NaClO_3 + NH_4ClO_4 \longrightarrow NH_3 + HCl + NaCl + 7/2\ O_2$$

From the mathematical application theoretically, can obtain an approximate value of the reaction temperature ($\Delta Hr = - 3.9$ kcal / mole).

Results and Discussion

The reaction mixture consisting of inorganic salts (sodium chlorate, ammonium perchlorate), iron filings as oxidizing factors, sawdust, activated charcoal, and distilled water, all work as an exothermic system.

Dependence of the temperature on the change in reaction components

From the results in tables (1 to 5), the ideal condition obtained in the reaction is the maximum temperature with a gradual or regular increase, the type of iron filings is important in increasing the speed of the reaction and heat generation at range (25-85 °C) and a diameter of the iron filing grains of 350 μ because the transformed of iron to its oxides, Fe_2O_3 and Fe_3O_4 needs a medium-sized diameter that not enabling iron filings to enter the grains or deposit inside the gaps which may stop or slow the oxidation-reduction reaction [12]. also, it was found a simple effect of the diameter of the sawdust grains, the best ideal condition (25 - 85 °C) corresponds to a diameter of 200 μ. The reason for that is sawdust in this physical state reduces the intense emission of heat and maintains a regulated height [13]. The change in the volume of distilled water does not affect the temperature, as indicated in table 4, while the type of charcoal has a role in increasing the number of adsorbed molecules (rate of adsorption) [14]. while changing the weight percentages of inorganic salts gives us the greatest effect among all the components of the mixture because both salts disintegrate into stable products such as sodium chloride (NaCl) and ammonium chloride (NH_4Cl) which disintegrate into ammonia gas (NH_3) and hydrogen chloride gas (HCl) [15]. Therefore, increasing the weight percentage of the two salts from 1: 1 to 3:3 gets temperatures of 25 - 85 °C and in a regular standard time (0-20 minutes). while the increase in the weight ratio to 4:4 or 5:5 leads to increases in the temperature but in a non-standard time. Therefore, the weight of sodium chlorate ($NaClO_3$) is important relative to the weight of ammonium perchlorate, so that the oxidation and reduction process takes place almost completely and an acceptable amount of heat is emitted.

It is difficult to follow the kinetics of oxidation-reduction reactions that involve a mixture of more than two substances due to the physical and chemical interaction of the substances with each other. the process of chemisorption of iron oxides (Fe_2O_3, Fe_3O_4) as well as the adsorption of carbon dioxide gas (CO_2) on the surface of activated charcoal or the sawdust suspended in the mixture contributes to giving a clear difference in the amount of heat emitted which calculated practically from the calorimetric method and the direct method of the Vant-Hoff equation.

The rate of the exothermic reaction

The reaction speed was not affected by the iron filings, sawdust, distilled water, and activated charcoal, these materials do not change the reaction speed and are considered auxiliary factors although the iron filings are considered a major reactant because it is oxidized by inorganic salts (chlorate ClO_3 and perchlorate ClO_4).

The speed of the exothermic reaction was measured based on the change in the concentrations of the two inorganic salts using classical kinetic methods for the reactants by deposition gravimetric analysis or the volatilization method, taking into account the reduction of interferences [16].

Order of reaction

By using the method of precipitation analyzing of ClO_3 radical in the potassium chlorate using the values obtained in table 7, the speed of the reaction depends on the radical or sodium chlorate meaning that n = 1 based on the proposed speed equation:

$$\text{Rate of reaction} = k\,[\,NaClO_3]^{\,n1}\,[\,NH_4ClO_4]^{\,n2}$$

It is possible to calculate the order of the reaction for ammonium perchlorate, using the volatility method, and from the results obtained from table 10, and11 it was found that n = 1, and thus the overall reaction is second-order for both salts.

The results obtained provide clear evidence for depending on the dissociation of the salts to give stable products and for their working in oxidizing the filings to iron oxides, or what is called self-dissociation [17], where it was found that the transformation of ($ClO_3 \rightarrow Cl$ or $ClO_4 \rightarrow Cl$) in the same substance overpowers the transformation of the filings into the corresponding oxides, so the emitted chloride ion was followed instead of the iron oxides [18].

Measurement of the heat released by the exothermic reaction

Using the Vant-Hoff equation to calculate the heat of the exothermic reaction is very important because it gives a clear image of the extent of the amounts of heat emitted with the spontaneous increase in the dissociation of inorganic salts.

It is noted that increasing the temperature led to increases in the speed of the reaction by increasing the specific velocity constant (k) by twenty times almost, from the initial temperature (t = 25 °C) to the final temperature (T = 85 °C), finding the value of the enthalpy gives real values for the heat emitted [19].

Enthalpy of calorimetric reaction

An actual comparison must be made between the calculations of the amount of heat for the exothermic reaction, between the direct application of the Van't Hoff equation, the use of the calorimeter, and conducting the direct reaction in a fixed volume, that is, under the same conditions. Hence, the enthalpy (Hr) depends on the quantity or number of grams of reactants causing heat generation and the total heat capacity (which is the calorimeter constant and the heat capacity of inorganic salts).

The measurements recorded in tables 12, and 13 found that the temperature increases by a small amount with time, calculating the calorimeter constant (C) found that the value of enthalpy (Hr) is less than the practical value for several reasons, the first is the short period to calculate the calorimeter constant and the second is the interference of other chemical materials in the mixture to absorb and emitted heat, such as the oxidation of activated charcoal to carbon dioxide gas [20].

Theoretical calculation of the enthalpy of exothermic reaction

The heat of the reaction emitted was calculated and appeared to exceed the calorimetric value and the practical value from Vant-Hoff equation due to several reasons, including the adsorption of components such as gas NH_3 and HCl on activated charcoal, in addition to the formation of ammonium chloride and some other secondary reaction during the reaction stages [21].

Conclusions

Based on the results of experiments on the exothermic reaction, conclude the following:

1 - The heat emitted from the dissolution of inorganic salts is controlled by oxidation-reduction reactions, also the presence of activated charcoal, sawdust, and iron filings is necessary to increase the speed of the reaction and to continue the adsorption of iron oxides deposited on the sawdust and activated charcoal.

2 - The speed of the exothermic reaction was determined and the reaction kinetics was studied based on the dissociation of sodium chlorate and ammonium perchlorate because part of the iron filings is adsorbed on the activated charcoal and the sawdust is not interring in the reaction and part of the activated charcoal is not consumed in the oxidation.

3-The heat emitted after measuring directly with the calorimetric method was found to be consistent with the temperatures used in thermochemical systems to be appropriate and beneficial in the applied aspect as well as the availability of these materials and their economic prices in addition to the purity of these reactions.

References

[1]   Sh. Mallakpour, F. Sirous, Ch. M. Hussain, Sawdust, a versatile, inexpensive, readily available bio-waste: From mother earth to valuable materials for sustainable remediation technologies, Advances in Colloid and Interface Science, volume 295, https://doi.org/10.1016/j.cis. 2021.102492.2021.

[2]   Alserai, SJ., Alsaraj, WK., and Abass, ZW., Effect of Iron filings on the mechanical properties of different types of sustainable concrete, open civil Eng. J. 12: 441–457. 2018.

[3]   Alzaed, AN., Effect of iron filings in concrete compression and tensile strength. Int. J. Recent Dev. Eng. Technol. 3(4):121-125. 2014.

[4]   Olaniyan, OS., Gbadero, OA., Obe, GS., and AbdulAzeez, MA., Influence of metal chips as a partial replacement for fine aggregate in concrete production. 4th International Conference on Engineering and Technology Research, Ladoke Akintola University, Ogbomoso. 23-25, 2016, pp. 227-235.

[5]   Adegoke, C.O., Available Alternative Energy Source for Domestic Use: A Case Study of Solar Cookers, Dryers and Sawdust Briquettes. Paper Work. 2003.

[6]   Alexandru, R.S., Putting Sawdust to Work in Romanian. Planet's Voice Article, Planet Voice Org. 2002.

[7]   Abdullah, Waleed R., Standard Sand Specifications Development by Mechanical Attrition Scrubbing to Make It Convenient for Cement Industry, Key Engineering Materials, Vol. 870, 2020, pp. 61-70.

[8]   M.A., Schneider, T. Maeder, P. Ryser, F. Stoess, A micro reactor-based system for the study of fast exothermic reactions in liquid phase: characterization of the system, Chemical Engineering Journal 101 (1-3), 241-250. 2004.

[9]   Dale, H., Huang, Thanh, N., Tran, Bao Yang, Investigation on the reaction of iron powder mixture as a portable heat source for thermoelectric power generators, 116:1047–1053 DOI: 10.1007/s10973-013-3619-9. 2014.

[10]   T., I., Shishelova, developing physical-chemical principles to manufacture effective heating systems when using mica, IOP Conf. Ser.: Mater. Sci. Eng. 667 012095, IOP Conference Series: Materials Science and Engineering. Doi:10.1088/1757-899X/667/1/012095. 2019.

[11]   Water Treatment and Conditioning of Commercial Heating Systems, Edition 1, Energy Association, www.icom.org.uk, @icomenergy. 2017.

[12]   Jean Brainard, Ph.D., Exothermic Reactions http://www.ck12.org/terms. 2014.

[13]   J. A. Hosely, J., Vanselow, R., Hower, R., Eds., Phys. of Solid Surfaces, VIII, Springer, Berlin. 1990.

[14]   D.Yoo, S.S. Shiratori, and M.F. Rubner, J. Am. Chem. Soc. 120, 7626. 1998.

[15]   G. Shaviv and N. J. Shaviva, J. Am. Chem. Soc. 529, 2000, pp. 1054 – 1069.

[16]   T. Livench and M. Asciler, J. Phys. Chem., B. 103, 5665. 1999.

[17]   Z. Aidom, and T. Marten, Apple. Therm. Eng. J., 22, 2002, pp. 1163 – 1173.

[18]   A. Kumar, Chem. Rev. J., 101, 2001, pp.1 – 19.

[19]   P. A. Grieco, Inorg. Chem. J., 133. 1993.

[20]   S. Sankarman, S. Neskamar and J.E. Roney, Envir. Chem. J. 57, P. 4. 2000.

[21]   S. Kumar and W. Wongsuwan, J. Appl. Phs. Vol. 34, 2001, pp. 660 – 666.