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Abstract

The machinery used to cool or freeze food uses a lot of energy. Consequently, it is necessary to lower energy use. Additionally, due to their significant global warming potential (GWP), traditional refrigerants must be replaced to help reduce greenhouse gas (GHG) emissions. Therefore, the usage of alternative refrigerants with lower GWPs is necessary. The possibility of the ammonium chloride ($NH_4Cl(s)$) and solid hydrated barium hydroxide ($Ba(OH)_2.8H_2O(s)$) based non-freon refrigerant as a substitute refrigerant was evaluated in this study. Demo-tests were conducted using a prototype refrigerator, which is essentially a closed chamber with foam and PVC insulation. Despite reaching the freezing point satisfactorily, the stirring chamber of the prototype had an unpleasant ammonia odor. Due to the lack of equilibrium between the reactant and product, these components were not permanent solutions like freons. Therefore, further research is needed to determine how effective it would be as a refrigerant.

1. Introduction

An electrical appliance called a refrigerator has a thermally insulated compartment and a heat pump that transfer heat, causing the temperature to drop as a result (Belman-Flores et al., 2015). In refrigeration systems, you'll usually encounter a compressor, a condenser, an expansion valve (capillary tube), and an evaporator (Ramesh Chandra Arora, 2011). All the pieces were connected to form a fluid circuit (Jeffery, 1989). Under lower pressures and temperatures, a liquid refrigerant evaporates to provide cooling. The outer cabinet and door, the inner cabinet or liner, the insulation positioned between the two, the cooling system, the refrigerant, and the fittings make up the basic components of modern refrigerators. The cabinet and door are made of aluminum or steel sheet metal, which is occasionally pre-painted. The internal cabinet is made of sheet metal or plastic, same like the exterior cabinet. Insulation made of fiberglass or polyfoam is used to fill the void between the interior and external cabinets. The cooling system's aluminum, copper, or an alloy (Ramesh Chandra Arora, 2011). Low temperature slows down the growth of bacteria, fungi, and other microorganisms, which lessens the rate at which food spoils. 3° to 5° C is the ideal temperature range for storing perishable food (Lewis et al., 2020). The freezing mechanism keeps the temperature close to the water's freezing point. Therefore, refrigeration is a crucial method of food storage that has been used for a long time (Deepika et al., 2011). Ice was used with food when it was first refrigerated, creating a natural freezing

compressor, condenser, coils, and fins are made of

was first refrigerated, creating a natural freezing mechanism. In the year 1834 AD, a vapor compression system-a method of artificially working freezing—was invented. Only until 1913 AD was it made available to the broader public. The market for freezing systems was enlarged with the advent of CFCls in the 1920s (Briley, 2004), however, it was subsequently discovered that CFCs were contributing to the ozone layer's thinning (Pussoli et al., 2012). Later, CFC-based freezing systems were no longer produced (Muller, 2021). A few years later, HCFCs



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were introduced as freons under the pretext that they wouldn't harm the ozone layer. Now, it is understood that HCFCs also contribute to global warming (Oxtoby et al., 2016). As a result of these facts, refrigeration technology is necessary in the world, as it has a lower environmental impact as well. As the world looks for environmentally acceptable and less disruptive solutions across all industries. The aforementioned reactant may hold promise for food storage and is less harmful to the environment than freons now in use. Therefore, more study and development are required to establish the aforementioned notion.

Theoretical background

An endothermic process in thermochemistry is any thermodynamic process that results in a rise in the system's enthalpy H (or internal energy U). A closed system often absorbs thermal energy from its surroundings during such a process, which causes heat transfer into the system. As a result, an endothermic reaction often causes the system's temperature to rise while the environment's temperature falls (Prather & Watson, 1990)

The reaction shown by the reagents are shown as follow:

 $2NH_4Cl(s) + Ba (OH)_2.8H_2O(s) \implies 2NH_3(aq) + BaCl_2. 2H_2O(s) + 8H_2O (De Fontaine, 2019)$

Heat from the environment was drawn into the chemical process. The chemical process heated up. The beaker and the bulk chemicals had the heat transported out of them (Tisza, 2009). The temperature of the surroundings drops when heat is moved out. Heat was emitted from the mixture into

the chemical process. Table 1 lists the thermochemical data for barium hydroxide, ammonium chloride, barium chloride, ammonia, and water.

Enthalpy of the reaction is calculated as:

$$\Delta H^{\circ} = \sum \Delta H^{\circ}_{f (product)} - \sum \Delta H^{\circ}_{f} (reactants)$$

$$\Delta H^{\circ} = 63500 \text{ J/mol}$$

Whereas entropy is calculated as

$$\Delta r S^{\circ} = \sum \Delta S^{\circ}_{f} (prod) - \sum S^{\circ}_{f} (reac)$$
$$\Delta r S^{\circ} = 368 \text{ J/K}$$

At standard condition free energy will be:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 63500 - 298(368) = -46100 \text{ J}$$

The hydroxide ion serves as the base in this neutralization process, and the ammonium ion serves as the acid. In the high entropy liquid and watery phases, the two comparatively low entropy crystalline solid reactants combine to produce many tiny molecules. A substantially negative free energy change (-47700 J/mol) results from this reaction because the positive enthalpy change (63600J/mol) is less than countered by the entropy change (368 J/mol.K) at ambient temperature. As a result, the reaction is endothermic and spontaneous (Scatchard & Prentiss, 1932). This process is endothermic. Energy conservation is the core principle of most calorimetry-themed exhibitions. Energy may be transferred, but it cannot be generated or destroyed that is:

$$q_{gain} + q_{lost} = 0$$

The reaction of ammonium chloride and barium hydroxide showed the of dropping the temperature up to -25°C (Scatchard & Prentiss, 1932).

Compound	$\Delta \mathbf{H}^{\circ}_{\mathbf{f}} (\mathbf{kJ/mol})$	S°298(J/mol·K)	ΔG°_{f} (kJ/mol)
NH ₄ Cl(s)	-341.4	94.6	-203
$Ba(OH)_2 \cdot 8H_2O(s)$	-3342	427	-2793
NH ₃ (aq)	-80.29	111	-26.6
H ₂ O(l)	-285.83	75.291	-237.2
$BaCl_2 \cdot 2H_2O(s)$	-1460.1	203	-1296.5

Table 1: Thermochemical data for barium hydroxide, ammonium chloride, barium chloride, ammonia, and water

2. Method

To check out the working of concept, a simple prototype was made.





water

Working

This prototype is made as simple as possible to see the working of the concept. It was made out of a closed chamber constructed out of plywood, foam, and aluminum foil. Beaker was in order to keep the regents. The motor-driven stirring mechanism was installed within the chamber that was made by adding the extension of plastic tube on the motor tube that mobilize the two solids in the beaker. When the stirring mechanism is activated, the chemicals react with each other which is an endothermic reaction that absorbs the heat with in the box thus lowering the temperature of the content as well as the surrounding environment.

Figure 1 helps to understand the construction of prototype and its different components. The box of prototype is made out of the plywood with the inner compartment of length 16 cm, breadth 16 cm and height of 46 cm. The plastic foam of 1cm thick was kept in all the inner portion of the box using fevicoal and the loose ends were sealed by liquid glue gun. The purpose of keeping the plastic foam beneath the ply-wood surface was to provide proper insulation from the external environment. Just beneath the plastic foam PVC carpet layer about 0.3mm thickness was used. It was adhered to the surface of plastic foam using fevicoal. The work for box was completed within 24 hours.

A plastic frame made of wiring box was used to provide frame to the 12 V DC motor. The length of frame was kept 14.8cm so that it would easily fit in to the box. For stirring extension of the motor plastic tube with 2 mm diameter was mounted to the shaft of the motor. the plastic pipe was made thicker from the bottom using the hot glue gun. The thicker bottom easily mobilizes the liquid. The wiring of DC motor was connected with 0.16mm thick PVC wire. The frame was then placed inside the box in height of 38 cm from the bottom. The wire was taken of the box from door area and sealed with hot glue gun. The wire was later connected with the 12-volt power supply. To start the mechanism solid barium hydroxide and ammonium hydroxide were kept in the beaker in a 3:1 ratio and beaker was placed inside the box. The door of the chamber was closed and gap that is seen when closing the door was sealed using the Vaseline making the box air tight. Then the adaptor was connected to the power circuit to start the working of the freezing system.

The prototype's interior chamber has a volume of about 3 liters. In different weight samples, a 3:1 mixture of solid barium hydroxide and ammonium chloride was utilized, and the maximum temperature drop inside the chamber was noted. To observe the cooling and freezing effects on objects outside the chamber, 50 cc of water was also placed within the chamber. Starting with solid barium hydroxide weighted at 30 grams and 10 grams of ammonium chloride, the chamber and water were monitored. The weight composition has been increased progressively as 2 times, 3 times till the optimal composition was achieved. For each composition of endothermic reaction 10 recordings were taken.

3. Results and Discussion

It has been found that the mass of the reagents used have direct relation of temperature drop within the chamber. The experimental results reveal a systematic analysis of the relationship between different NH₄Cl to Ba(OH)₂ weight ratios and temperature fluctuations within the 3 lit chamber (C) and 50 gm of water (W). As the weight ratio climbs from 10:30 to 50:150, the temperature of the chamber and the water lowers slowly and gradually. The temperature in the chamber consistently drops; the largest drop, which reaches a minimum of -3° C is observed for the 50:150 composition.

	Different Compositions										
Weight ratio(gm)	10	10:30		20:60		30:90		40:120		50:150	
NH ₄ Cl:Ba(OH) ₂											
	С	W	С	W	С	W	С	W	С	W	
	19	22	16	18	10	12	2	4	-2	0	
	21	23	16	19	9	11	2	4	-1	1	
Temperature	21	22	17	18	8	10	3	5	-2	0	
reading in ⁰ C	21	23	17	18	10	12	2	4	-3	-1	
	21	22	16	19	9	12	3	4	-2	0	
	21	23	16	19	8	10	2	3	-2	0	
	20	22	17	18	10	12	2	4	-1	1	
~ ~ ~	20	22	16	18	10	11	2	4	-3	0	
C: Chamber	21	22	17	19	9	12	3	5	-2	0	
W: Water	21	23	16	18	8	10	3	5	-2	1	

Table 2: Temperature drop observed in different composition sample studies

The drop in temperature is sharp and steady from 20:60 to 30:90 to 40:120 weight ratio of NH₄Cl to Ba(OH)₂. However, the decrease is not as much when we reach 50:150 weight ratio NH₄Cl to Ba(OH)₂. It suggests that the rate of decrease in temperature for higher weight ratios of NH₄Cl to Ba(OH)₂ goes on

decreasing as weight of NH_4Cl and $Ba(OH)_2$ is increased gradually and finally reaches an optimum minimum value up to which the temperature of chamber could be cooled at minimum. So, further researches are necessary.



Figure 2: Graph of average drop on the temperature in chamber and water at different composition where the horizontal lines are 1-temperature of prototype of empty chamber,2 – temperature drop at 10:30 composition; 3-temperature drop at 20:60 composition; 4- temperature drop at 30:90 composition ;5 temperature drop at 40:120 composition; 6- temperature drop at 50:150 composition.

However, actual applications must examine the feasibility and scalability of adopting such compositions, while also addressing the technological limits. The observed trends provide a foundation for further optimization and refinement of the mixture's composition to achieve more efficient and controlled temperature drops. Ammonia that had escaped from the conical flask and couldn't be converted back into ammonium hydroxide is the current problem during the procedure. However, by modifying the apparatus, the ammonia thus produced can be used. The response back and forth test was impracticable as ammonia that was discharged diffused around the room and produced a highly grating impact. We might not have the smell issue if the recommended combination had been utilized in a closed vessel.

The temperature in the prototype dropped for around 20 minutes, or until all of the solid reagents had become watery or until all of the reactants had produced a product, before rising again. If it can be reused over a long length of time due to the equilibrium reaction between the reagents, the mixture of ammonium chloride and barium hydroxide in a sink can be an alternative as an environmentally friendly freezing element. The freezing effect that has been present for a while may be resolved if we can somehow restore the reactants. This technique may be a more cost-effective freezing solution. Hence, future research should explore the underlying mechanisms governing the reactions to enhance the applicability of the proposed system.

4. Conclusion

Ammonium chloride and barium hydroxide mixed together have the potential to replace freons, which are currently employed in freezing applications. When 200 gm of these reagents were utilized, the freezing potential of the reagent reached a maximum of -3°Cin a 3-liter chamber, which is an essential aspect to consider. The expected result of obtaining long term usage of the reagents couldn't be achieved as the ammonia had leaked from a conical flask and couldn't be changed back into ammonium chloride. Apart from this downside it is also worth to note that the power consumption was very low because the major powerusing component is only a stirring mechanism and the result points depending on energy usage, the method could be more affordable. Hence, further research and testing is needed to fully assess the feasibility of using this technique as a replacement for freons in freezing application.

5. Conflicts of Interest

The authors declare that they have no competing interests.

6. References

- Belman-Flores, J. M., Barroso-Maldonado, J. M., Rodríguez-Muñoz, A. P., & Camacho-Vázquez, Enhancements in G. (2015). domestic refrigeration, approaching sustainable а refrigerator-A review. Renewable and Sustainable Energy Reviews, 51, 955-968.
- Briley, G. C. (2004). A history of refrigeration. Ashrae Journal, 46, S31-S34.
- Chandra, A. R., & Arora, R. C. (2011). Refrigeration and air conditioning. PHI Learning Pvt. Ltd..
- Deepika, G., Rastall, R. A., & Charalampopoulos, D. (2011). Effect of food models and lowtemperature storage on the adhesion of Lactobacillus rhamnosus GG to Caco-2 cells. *Journal of agricultural and food chemistry*, 59(16), 8661-8666.
- De Fontaine, D. (2019). Principles of classical thermodynamics: applied to materials science.
- Lewis, G. N., Randall, M., Pitzer, K. S., & Brewer, L. (2020). Thermodynamics. Courier Dover Publications.
- Maxwell, J., & Briscoe, F. (1997). There's money in the air: the CFC ban and DuPont's regulatory strategy. Business strategy and the environment, 6(5), 276-286.
- Müller, M. (2021). The contributions of animal agriculture and major fossil-fuel-based industries to global warming.
- Oxtoby, D. W., Gillis, H. P., & Butler, L. J. (2016). Principles of modern chemistry.

- Prather, M. J., & Watson, R. T. (1990). Stratospheric ozone depletion and future levels of atmospheric chlorine and bromine. Nature, 344(6268), 729-734.
- Pussoli, B. F., Barbosa Jr, J. R., da Silva, L. W., & Kaviany, M. (2012). Heat transfer and pressure drop characteristics of peripheral-finned tube heat exchangers. International journal of heat and mass transfer, 55(11-12), 2835-2843.
- Tisza, L. (2009). Adventures of a theoretical physicist, part I: Europe. Physics in Perspective, 11, 46-97.
- Jeffery, G. H. (1989). Quantitative chemical analysis. New York.
- Scatchard, G., & Prentiss, S. S. (1932). The freezing points of aqueous solutions. III. Ammonium chloride, bromide, iodide, nitrate and sulfate. *Journal of the American Chemical Society*, 54(7), 2696-2705.