Microwave Technology: An Effective Approach to Rapid Material Synthesis

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Abstract

Microwave technology is useful in materials science due to its ability to focus energy to achieve consistent reaction conditions, which are difficult to obtain under normal laboratory settings. During these reactions, water can be heated above its boiling point while the temperature-pressure relationship of this super heated liquid is monitored. It has been demonstrated through water tests that the instrumental temperature-pressure data agrees with theoretical results to confirm the accuracy of this method. One project currently being undertaken with this technology is the synthesis of $MgFe_2O_4$, which takes advantage of the microwaves' capabilities for finely tuning reaction parameters to yield desirable results. XRD data has confirmed the success of this synthesis and can be used to study products from future manipulations of reaction conditions.

Background

Figure 1: The Discover SP Microwave Synthesis System

- •Used since the 1950s mainly for organic synthesis.
- •Recent interest in utilization for inorganic reactions
- •Easy to use
  - •Programmable
  - •Automated for multiple reactions
  - •Very few, easy to understand parameters for operation
- •Current microwave systems are too expensive for ubiquitous use
- •Not applicable to all industrial processes yet; only small reaction volumes can be used

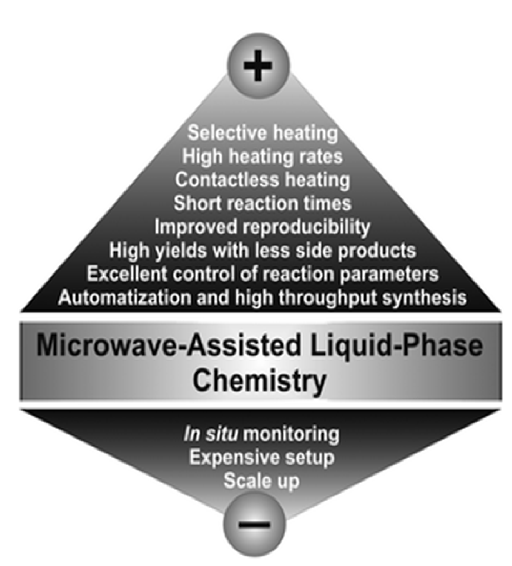
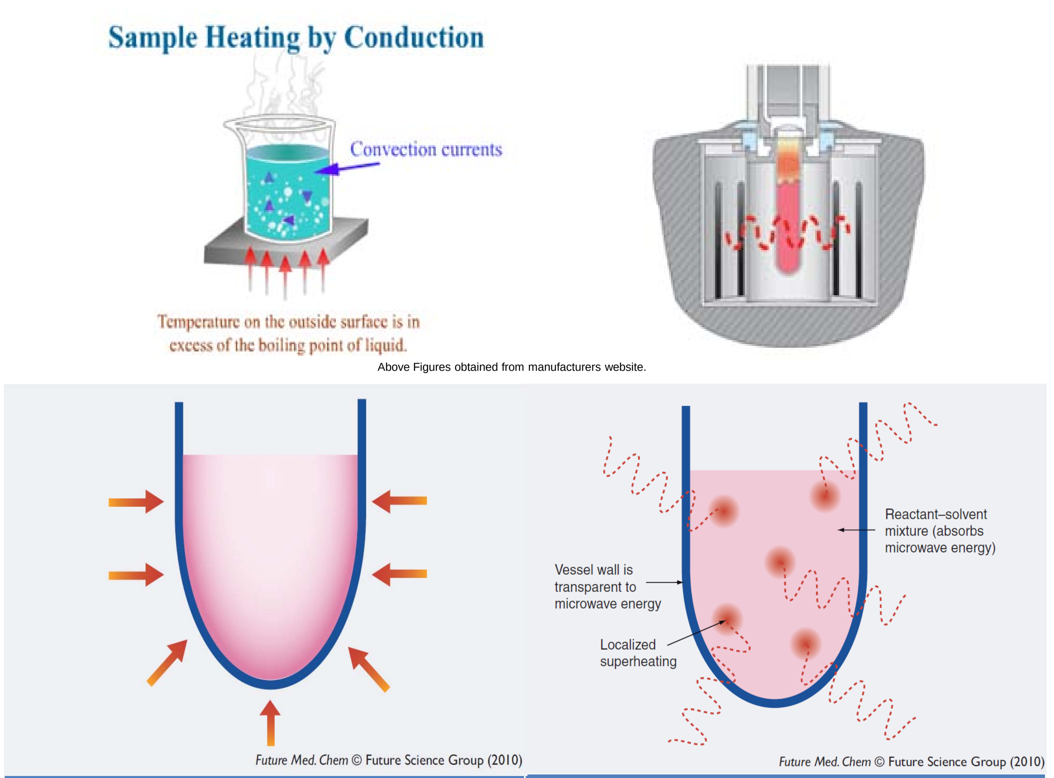


Figure 2: Advantages and disadvantages of microwave synthesis.

Background

Figure 3: Conventional heating vs. microwave heating



Conventional	Microwave
•Inconsistent heating → temperature variation in solution	•Microwaves absorbed throughout solution → mostly homogenous heating
•Performed under atmospheric conditions → limits temperature and pressure conditions	•Performed in sealed vessel under extreme conditions → temperature and pressure can reach superheated conditions

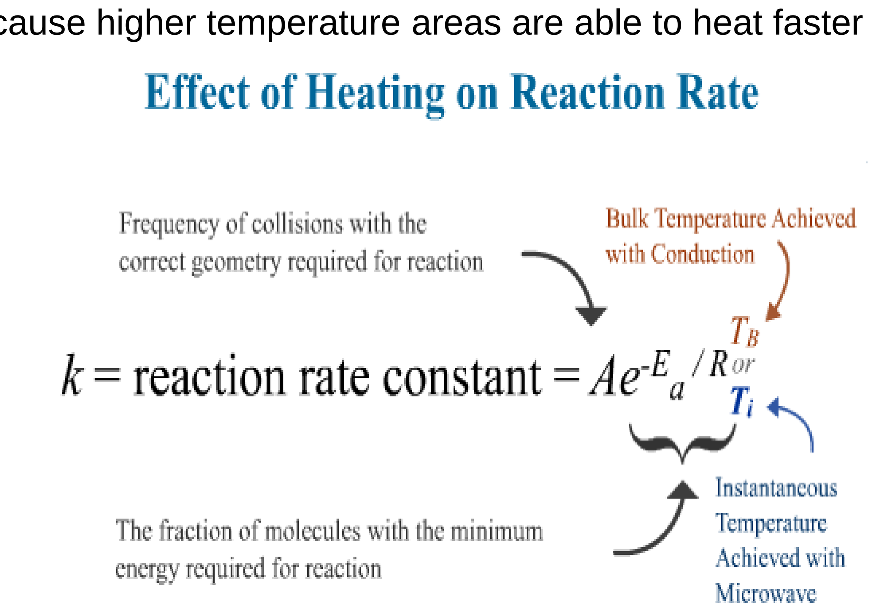
•Microwave radiation does not have enough energy to break bonds

•Microwaves induce rotational motion in molecules

•Mechanism of heating is that molecules orient their dipole moment along oscillating electric field. Collisions between the molecules are much faster than rotations

•Collisions and friction between water molecules produces thermal energy

•Some inorganic materials susceptible to thermal runaway: The dielectric constant, which is dependent on temperature, determines rate of heating. This can cause localized points of superheating because higher temperature areas are able to heat faster



Kinetics of reactions using microwave heating are an important advantage

- •Microwave heating can be applied or turned off instantly, allowing for precise experimental control
- •Heating is achieved rapidly compared to conventional methods
- •Superheated reaction mediums means unique kinetics can be explored
  - •Arrhenius kinetics- ~every ten degrees doubles rate of reaction

Water tests

•In order to take advantage of the precision microwave instruments provide, the temperature and pressure monitors within the instrument must be precise.
•Cross referencing of temperature and pressure data for a pure solvent with known thermodynamic data (e.g. water) provides a method for calibration and investigation into the accuracy of the temperature and pressure probes

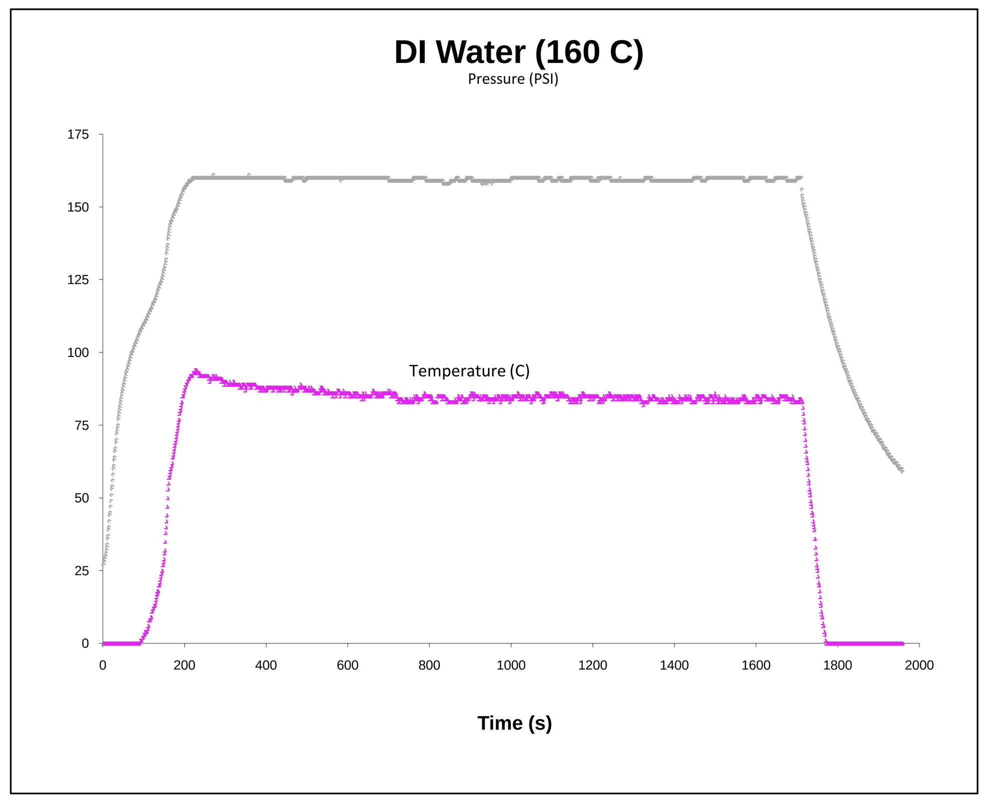


Figure 4: Sample water test showing temperature/pressure relationship for water.

Observed Temperature	Pressure
160°C	Observed: 84 PSI
	Expected value: 90 PSI

Figure 5: An example of the difference between the measured temperature/pressure relationship of water and the expected literature values.

There is inconsistency between measured temperature/pressure data and literature temperature/pressure data, but the values are relatively close.

The instrument is measuring pressure directly, but measuring temperature indirectly (i.e. an infrared sensor).

This inconsistency would be relevant to kinetic studies of reactions carried out with this instrument, and results must factor this error into account.

Experimental

$$Mg^{2+} + 2\,Fe^{3+} + 4\,H_2O \rightarrow MgFe_2O_4 + 8\,H^+$$

$Fe(NO_3)_3$ and $Mg(NO_3)_2$ are combined in a 2:1 ratio and dropped into excess KOH. The reaction is carried out in a Discover SP microwave for varying amounts of time and at different temperatures (typically around 150°C for 30 minutes).

The product is washed, ground and packed for analysis using power X-Ray Diffraction.

Results

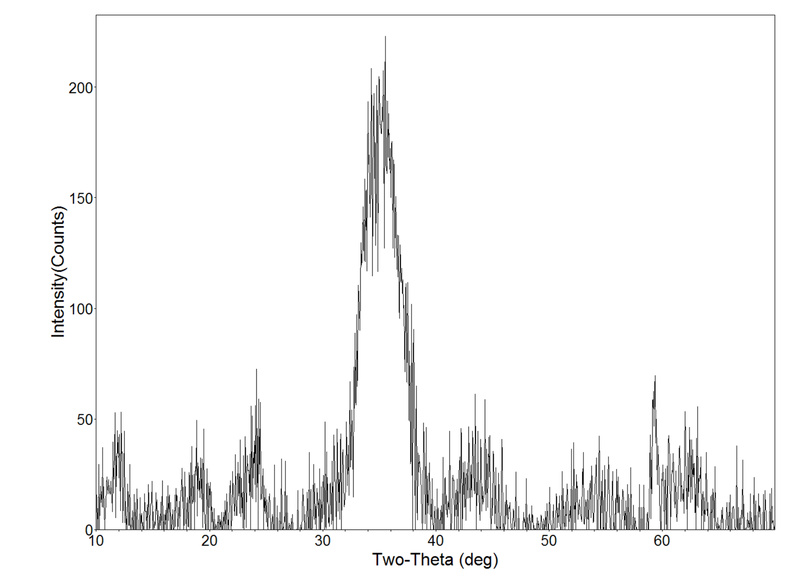


Figure 6: Experimental XRD pattern for $MgFe_2O_4$.

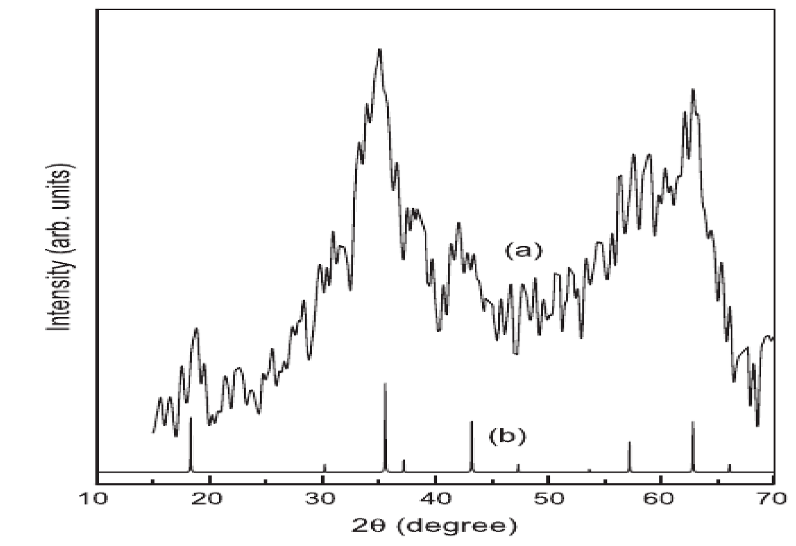


Figure 7: Literature XRD pattern for $MgFe_2O_4$.

There is agreement between experimental and literature patterns. However, the signal to noise ratio in both patterns is not ideal, suggesting small crystallite size.

Conclusions

Microwave instruments are a novel piece of technology that provide many practical advantages for inorganic synthesis. The nature of this instrument provides advantages over conventional heating, especially the ability to reach superheated conditions. Thus it is important to precisely determine the temperature and pressure relationship within the reaction vessel. Although the temperature and pressure probes show some inconsistencies compared to theoretical values, this is most likely due to the method used to measure these values.

Preliminary studies of $MgFe_2O_4$ show promising results. Future studies will center on further variation of reaction conditions using the microwave to change crystal properties of the material. After the synthesis is optimized, this material will be tested electrochemically for applications as a cathode in batteries.

References

1. Collins Jr, M. J., Future trends in microwave synthesis. *Future Medicinal Chemistry* ***2010, 2 (2), 151-155.***
2. Loupy, A., Ed.; In Microwaves in Organic Synthesis;Wiley-VCH Verlag GmbH & Co:Weinheim, **2002.** pp 1-73.
3. Galema, S. A. Microwave Chemistry. *Chem. Soc. Rev.* **1997**, *26*, 233-238.
4. Verma, S.; Joy, P. A.; Khollam, Y. B.; Potdar, H. S.; Deshpande, S. B., Synthesis of nanosized MgFe2O4 powders by microwave hydrothermal method. *Mater. Lett.* ***2004, 58.***

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