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Jeremy Hardinger

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Reactions of Metal Carbides to Produce Carbon

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Dissertation submitted
to the Statler College of Engineering and Mineral Resources
in partial fulfillment of the requirements for the degree of

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Abstract

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Calcium carbide was historically used to reduce potassium metal from potassium fluoride as described in a 1922 patent. This was prior to the discovery of electrolytic synthesis, which replaced the carbide process in less than five years. A byproduct of this process was elemental carbon. This carbon was unanalyzed at the time. The object of this research was to analyze carbon produced in reactions similar to this and to determine if this reaction could be carried out under milder conditions. It was found that the reaction is part of a family of reactions, and would proceed with a number of other salts, including zinc chloride, stannous chloride, and stannous fluoride. The carbon produced via molten salt reactions was irregular, and primarily amorphous. The reactions could take place in a solvent at room temperature. Carbon produced via solvent-phase reactions was more orderly and primarily graphitic. Finally, the reactions could take place in a galvanic cell, separating the reactions into two half reactions. This configuration had numerous benefits: reaction rates could be measured via current, metallic byproducts are produced in a separate cell from carbon simplifying purification, and morphology of carbon was more regular. Almost no amorphous carbon was produced in this configuration. The carbon produced in solvent-phase reactions, both simple solvent-phase and galvanic cell, showed unusual morphology. Highly ordered, hexagonal crystals were found throughout all solvent-phase reaction products. These crystals were shown to be highly ordered via Raman spectroscopy. Future work should be focused on synthesizing carbides to reduce contaminant concentration, synthesizing commercially unavailable carbides, and attempts to isolate and exfoliate hexagonal crystals to graphene.

Prelude

This dissertation reports on a research area that has largely been ignored in past. Its focus is on a historical method for producing potassium metal. A side product of that reaction was elemental carbon, described as “graphite”. The basic information of this chemistry is described in a series of patents, but no proof was provided to support the claim that the carbon was actually graphite. Soon after the process was patented, the electrolysis of molten salts proved to be a more efficient method for producing potassium, thus the chemistry was “lost to history”.

Recently, there has been an increased interest in carbon, and this research was directed towards using this chemistry as a new avenue to carbon allotrope synthesis. Because there is essentially no literature to review, the dissertation begins with a “Statement of the Problem”, which concludes with a series of questions which are to be addressed. This is followed by a research plan. The research plan addresses the questions and designates specific tasks which define the approaches used to answer the proposed questions. This is followed by a discussion of the analytical techniques which are the most appropriate for carbon allotrope identification. At first, this might seem out of place, but this background is necessary to follow the research program and its development. Note that while this is the same content proposed in *Proposal*, it is in a different order, thus the description of tasks is not in the same order as the Research Plan tasks. Literature and background information appropriate to the tasks are presented at the beginning of the tasks. Experimental activity is described in the middle

of the tasks, and conclusions are found at the end of the tasks. The four questions presented in the statement of the problem are addressed in this manner.

At the end of the dissertation are statement of final conclusions and a description of the specific achievements of this work. This is followed by recommendations for research to continue this research program.

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1. Statement of Problem

The basis for this research is a largely unexplored reaction, patented in 1919, to manufacture potassium metal via the reaction below: U.S. Patent # 1,319,148¹

This reaction takes place heterogeneously at 860°C, just above the melting point of KF (858°C).² At this temperature potassium is vaporized and is condensed out onto a cold finger above the reaction medium. Carbon was reported as graphite, and calcium fluoride formed a slag on top of the molten salt. Shortly after the discovery of this reaction, cheaper, more efficient electrolytic processes were invented to produce reactive metals³. Consequently, this process has been left relatively unexplored since then. Examination of the reaction shows that it is classified a redox reaction. The carbide anion is oxidized to elemental carbon while the metallic cation is reduced to elemental metal. The exact nature of the carbon produced was not documented. This led to a question, can this or similar reactions be used for the manufacture of specific carbon allotropes instead of just producing potassium metal?

2. Object of Research

Carbon is one of the most interesting and versatile elements in existence. Its ability to bond indefinitely with itself allows the formation of both purely carbon crystals (fullerenes) and a nearly limitless variety of organic and inorganic compounds. Naturally, pure carbon exists as one of two allotropes: graphite and diamond. In recent decades, other allotropes have been invented. These include carbon nanotubes, buckminsterfullerene⁴ (Bucky balls), and graphene⁵. All of these synthetic allotropes consist of the same sp^2 hybridized bonding system found in graphite. This means that they are all sheets of graphite formed into different shapes: a cylinder forms carbon nanotubes⁶, a ball forms Bucky balls, and a small number of sheets forms graphene. The methods for forming different allotropes include high-temperature/high-pressure growth⁷, chemical-vapor deposition⁸, mechanical exfoliation⁹, and many other methods. But no one has explored the reactions of carbides for the synthesis of any carbon allotropes. The objective of this research is to test that possibility.

3. Research Plan

The research described in this proposal evaluates the reactions of carbides by metal halide salts to produce elemental carbon. The production of potassium metal was accomplished by reduction using calcium carbide¹. Elemental carbon was one of the other products of this reaction. The goal of this research is to evaluate the use of such carbide oxidation reactions to produce various allotropes of carbon. The research is divided into five primary tasks:

- (1) The selection of the most suitable carbide and metal halides to be used based on commercial availability, reactivity, and physical properties of the materials.
- (2) Determine if these reactions can be accomplished in media other than molten salts
- (3) Characterize the products of reaction. This will involve SEM-EDS, XRD, optical microscopy, particle-size analyzer, and Raman spectroscopy.
- (4) Development of a system in which the products of the reaction can be isolated for easy analysis and the effects of changing parameters can be evaluated
- (5) Develop a control method so select allotropes can be produced.

3.1. Task 1 Selection of Carbides and Metallic Halide Salt

Almost all elements react with elemental carbon to form carbides. Carbides come in several varieties: salt-like, covalent, interstitial, and complex¹⁰.

Covalent Carbides

Covalent carbides include silicon carbide, SiC , and boron carbide, B_4C . These compounds are almost chemically inert at most temperatures. They are known to be refractory¹⁰, and incredibly hard. Because of their inert nature, covalent carbides are not expected to be reactive. However, silicon carbide is inexpensive and readily available, so it will be tested. Because of its inert nature, silicon carbide may require reaction with more reactive salts, salts that would not otherwise be considered.

Interstitial carbides

Interstitial carbides are transition metals with carbon atoms in the interstices of the metal lattice. These carbides are also hard, and refractory, and are also not reactive at most temperatures¹⁰. Thus, they are removed from consideration as a reactant.

Complex Carbides

These carbides resemble interstitial carbides but they have some chemical reactivity¹¹. In dilute aqueous acid solutions, they react to form simple hydrocarbons. However, these complex carbides do not follow chemical valance rules. Typical examples are Fe_3C and Cr_7C_2 . Because of the complex nature of these carbides it was decided not to study them in this research.

Salt-like Carbides

Salt-like carbides contain a metal cation and a carbide anion. Salt like carbides follow chemical valance rules and react with water to produce hydrocarbon gases and metallic hydroxides¹². Salt-like carbides can be categorized based on the valence of the carbide anion. The categories of salt-like carbides are named for the gas produced upon reaction with water. (1) Methanides produce methane, CH_4 . The methanide carbide

anion is C^{4-} . Methanides include aluminum carbide, Al_4C_3 , magnesium carbide, Mg_2C , and beryllium carbide Be_2C . (2) Acetylides form acetylene (ethyne), C_2H_2 , upon contact with water. C_2^{2-} is the acetylide carbide anion. Acetylides include calcium carbide, CaC_2 , and lanthanum carbide, LaC_2 . (3) Sesquicarbides produce propyne, CH_3CCH , and propadiene, CH_2CCH_2 , upon contact with water. C_3^{4-} is the sesquicarbide anion. Lithium, Li_4C_3 , and magnesium, Mg_2C_3 , are the only metals known to form sesquicarbides. The table below summarizes the salt like carbides and the gases produces as a result of reaction with water. Because salt-like carbides are the most likely to be applicable, details of the synthesis of each salt-like carbide must be considered. This is important because some salt-like carbides have no high-purity forms available, and the contaminants are a result of the synthesis route.

Table 1 - Salt-Like Carbide Summary

Carbide Name	Carbide-Anion	Examples	Gas evolved
Methanides	C^{4-}	Al_4C_3 , Mg_2C , Be_2C	CH_4
Acetylides	C_2^{2-}	CaC_2 , LaC_2 , Li_2C_2	C_2H_2
Sesquicarbides	C_3^{4-}	Li_4C_3 , Mg_2C_3	CH_3CCH , CH_2CCH_2

Salt-Like Carbide Synthesis

Aluminum carbide is produced primarily in an electric arc furnace from the elements at temperatures of approximately 1800°C. Carbon is introduced in the form of a graphite electrode which is consumed¹³.

Aluminum carbide has a high hardness and has been used as an abrasive¹⁴. However, it reacts with moisture in air, so its uses in this application are limited. A low demand combined with difficult synthesis result in aluminum carbide being available at lab scales, but not at industrial scales.

Magnesium carbide has been synthesized from the elements on lab scales.

MgC_2 is not thermodynamically stable at low pressures. It requires very high pressure ($\sim 10 \text{ GPa}$) to form via synthesis from the elements¹⁵. Because of this, MgC_2 is not available to purchase.

Beryllium carbide is produced from beryllium oxide. The oxide is reacted with coke in an electric arc furnace at 2000°C ¹⁶.

Beryllium carbide and beryllium oxide are both toxic when inhaled as fine powders.

Because of this, and its low commercial availability, beryllium carbide has been ruled out as a potential carbide.

Calcium carbide is produced similarly to beryllium carbide from calcium oxide (lime) and coke in an electric arc furnace at approximately 2000°C ¹⁷.

This process uses the metal oxide rather than the reduced metal, which makes calcium carbide considerably cheaper to manufacture than aluminum carbide. Moreover,

calcium carbide has an industrial demand as a pathway to acetylene from carbon¹². This means that calcium carbide is inexpensive and already available on an industrial scale. Lanthanum carbide can be synthesized from the elements or from lanthanum oxide in an electric arc furnace¹⁸.

Its primary use is currently lab-scale, semi-conductor research¹⁹. Because of the low demand, it is not available commercially.

Lithium carbide is produced by reacting molten lithium metal with graphite at high temperatures (~1330°C) with graphite in a carbon dioxide atmosphere²⁰.

It can also be produced by reacting lithium carbonate with graphite in an electric arc furnace²¹.

Lithium carbide is not commercially available.

Lithium sesquicarbide is produced by reacting lithium chloride with graphite at approximately 900°C²².

Lithium sesquicarbide is not commercially available.

Magnesium sesquicarbide is produced by bubbling methane through molten magnesium metal at approximately 700°C²³.

Magnesium sesquicarbide is not commercially available, but can be produced with common lab equipment. However, it is by far the most reactive carbide with water.

Literature on the characterization of magnesium carbide (XRD) is scarce.

To summarize, salt-like carbides are the only reactive variety of carbide. Of these compounds, calcium carbide and aluminum carbide are readily available commercially, while magnesium sesquicarbide can be synthesized with common lab equipment. All other carbides are not available commercially and require highly specialized lab equipment to synthesize.

Salt Selection

The reaction shown in Equation 1 is interesting because it shows that calcium carbide is a powerful reducing agent, capable of reducing the potassium cation, which has a standard reduction potential of -2.936 V^{24} .

Potassium has the second lowest (most negative) reduction potential (lithium having the lowest). After observing the powerful reducing nature of calcium carbide (see Reaction (1)), it was hypothesized that a similar reaction could take place at lower temperatures if a more easily reduced metal were used in place of potassium and the halide salts of these metals had lower melting points. It is hypothesized that this may allow for the morphology of the carbon produced to be controlled because the different states of carbon would be produced at different voltages. Varying the metallic cation

reduction potential and melting point would vary the voltage, as per the Nernst Equation (discussed in the Appendix). Graphite is the most thermodynamically stable form of elemental carbon, so it makes sense that at high temperatures, graphite would be formed. But at lower temperatures and milder reduction potentials, the carbide anion may not have enough energy to change hybridization, and thus might retain its hybridization through the reaction to produce less stable states of carbon. In order to test both carbide reactivity and changes in morphology, the proper salts need to be identified.

For the reaction to take place in this manner at lower temperatures, the metallic halide salt must have a lower melting point and by using a metallic cation with a more positive reduction potential the oxidation of the carbide anions might not require the resulting carbon to be at its most stable state. In order to test our hypotheses, a salt is needed that: (1) contains a cation with a high (less negative) reduction potential, and (2) has a low melting point. The salt must also be compatible with common handling materials (glass or metal). It is known that fluorides are highly corrosive to metals and dissolve glass. They tend to have very high melting points. In spite of this, a few experiments will be done to evaluate fluoride salts, but the primary focus will be on chloride salts.

Table 2 includes a summary of all potential candidates for salts to be used in the proposed research.

Table 2 - Salt Candidates

Reduction Half-Reaction	Standard Potential (V)	Formula	m.p. of chloride (°C)
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04	LiCl	605
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92	KCl	770
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.76	CaCl_2	772
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71	NaCl	801
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.38	MgCl_2	714
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66	AlCl_3	192
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76	ZnCl_2	292
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74	CrCl_3	1152
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.41	FeCl_2	677
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.4	CdCl_2	564
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.23	NiCl_2	1001
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14	SnCl_2	247
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13	PbCl_2	501
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.04	FeCl_3	306
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34	CuCl_2	498
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	0.52	CuCl	426
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.8	AgCl	455
$\text{Hg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Hg}(\text{l})$	0.85	HgCl_2	276

Based on Table 2, the chlorides considered are zinc chloride, stannous chloride, and ferric chloride. The only fluoride considered is stannous fluoride. All other salts are either too difficult to reduce (high reduction potential) or have a melting point that is too high. (Mercurous chloride has been removed from consideration for multiple safety

reasons. Mercury metal is toxic, and mercury is known to form explosive compounds with carbon.)

To summarize, the potential carbides are aluminum carbide and calcium carbide.

Potential salts are zinc chloride, stannous chloride, and ferric chloride. Potential reactions include:

Experimental Procedure to Test Molten Salt Reactions

The proposed reactions will follow the patent from 1919, and will use pure compounds

(no solvent). Molten chlorides rapidly corrode most metals²⁵, so metal reactors cannot

be used. This is not a large setback as a low reaction temperature is desired, so glass-

lined (borosilicate) reactors will be used. All of the reactants either react with water, are

hygroscopic²⁶, or both. Because of this, the reactors must be charged in a highly-

controlled environment. A glove box with an argon atmosphere will be used.

It is desired to have homogeneous reaction conditions, so the reactants must be charged as a well-mixed powder. Aluminum carbide is available as a fine powder. The salts are all available as fine powders. Calcium carbide is only available as large (~2 cm) pieces. Calcium carbide must be crushed to an even size. To do this, a mortar and pestle will be used in conjunction with standard sieves. The calcium carbide will be crushed to a size between 100 mesh and 200 mesh (0.15 mm – 0.075 mm).

Once the reactants have been prepared, they will be weighed out, mixed, and loaded into a 1" ID, 5" long borosilicate test tube. The tube will then be placed into a stainless steel tube, which will be sealed with high-temperature sealant and end caps. Aluminum chloride is the only compound with an appreciable vapor pressure at the temperatures²⁷ used (nearly 10 atm. at zinc chloride's melting point). The sealant and stainless tube will easily withstand this pressure.

Once sealed, reactors will be placed into a furnace. It is believed that mass transfer will be severely limiting, such that no reaction takes place below the melting point of the salt. Taking advantage of that, the reactors will be heated to 5°C below the melting point of the salt and held there for 5 hours to allow for the contents to homogeneously heat. Then, the furnaces will be taken quickly to the final temperature and held for the desired time. The reaction time will be defined as the time the reactors are above the melting point of the salt. Once the reaction time has expired, the furnaces will be turned off.

After sufficient time has passed to allow the reactors to cool, they can be removed from the oven. Since carbon is the only compound of interest, it is no longer necessary to control the atmosphere that the products are exposed to. (Carbon does not react with any compounds present at ambient temperatures.) The reactors can be opened, and the cleaning procedure can begin.

Cleaning Procedure

Potential byproducts include all reactants and products excluding carbon, and any new compounds formed as a result of additional reactions that occur either with the environment or with cleaning agents. Fortunately, carbon is highly stable at room temperature as amorphous carbon, graphite, and diamond, so strong cleaning agents can be used.

Carbides – the carbides can be removed by reaction with water, as per Equations 23 and 24. This reaction produces new byproducts, calcium and aluminum hydroxides, which are both soluble in acid.

Salts – the salts are all soluble in water. Stannous chloride reacts with hot water to produce the basic chloride $\text{Sn}(\text{OH})\text{Cl}$.

Using cold water, however, is not an option. The salt has a high heat of solvation, and any unreacted carbide will react with the water exothermically, precipitating out the basic chloride. To remove the chloride, acid must be used to shift the equilibrium to the left.

Metals – the pure metals produced all react with acid to form hydrogen and a salt (which is soluble in water). However, the metals formed could have a very high surface area, which means that they could rapidly form an oxide before acid contacts them.

Metal oxides – The metal oxides all react with acid to form soluble products except for tin dioxide. Tin dioxide reacts with hot, concentrated potassium hydroxide to form soluble products.

To summarize, the products will be exposed to water, then filtered or centrifuged to remove any remaining carbide and salt. Then, the products will be exposed to acid to remove any metals and hydroxides formed in the previous step, and filtered. Next, potassium hydroxide will be used if the reaction contains tin to remove any tin dioxide, and filtered. Finally, the products will be washed with methanol to dry the now pure carbon, and filtered.

3.2. Task 2 Selection of Potential Solvents

The primary reason that the salt must be molten is in that state the ions are free to move and react. Another method for producing free ions is to dissolve the salts in a solvent. Task 2 of this research is to determine if reactions of this type can be done in solution at ambient temperature. In this situation, the salt would be dissolved rather than melted to ionize it and increase mass transfer. Different parameters would become important when using a solvent. Solubility of the salt, compatibility between the solvent and the carbide selected, and certainly many unforeseeable parameters would be important. It is not certain, at this stage, if the reaction can proceed in the solvent

phase. However, if the reaction does occur in the solvent phase, concentration, in addition to temperature, could be used to control the oxidation potential. This would be much more practical, experimentally. For this to be tested, potential solvents must be unreactive with the carbide anions and still have appreciable solubility for the metallic salts. Therefore, the solvents must have no or no significant acidity. Furthermore, the solvents must be difficult to reduce. Potential candidates are acetone, methanol, ethanol, NMP, tetrahydrofuran and acetonitrile. Tests will be run to determine that stability of the salt like carbides in these solvents as well as the salt solubility.

The solvent phase experiments will consist of four preliminary steps:

1. Selection of potential solvents
2. Determine solvent-carbide compatibility
3. Determine solubility of salts in carbide compatible solvents
4. Determine which reactions occur with soluble salts in compatible solvents

(1) First, a series of solvents must be selected. The solvents must ionize salts and must not attack carbides. Literature on the compatibility of solvents with carbides is sparse, and literature on solubility has been shown to be inaccurate. However, basic knowledge of chemistry can limit the number of solvents considerably. Carbides are attacked by protons, so the solvent must have a low acidity. Typical non-aqueous electrolytes include acetone, alcohols, and acetonitrile. For the purposes of this research, acetone, methanol, ethanol, and acetonitrile will be used. Longer alcohol chains will not be used because although they are less acidic, they tend to be less capable of dissolving the salts

of interest. More exotic solvents will also not be considered for economic reasons (This research is funded with the intentions of developing an industrial process.). (Note: these solvents are all hygroscopic. Any inclusion of water will cause the undesired side reaction to occur, so solvents will be distilled and dried with molecular sieve.

Acetonitrile, however, attacks many polymers. It is, at present, unclear if acetonitrile can be safely handled at the available facilities.)

(2) The solvent must be shown to be compatible with the carbide. The carbides to be used react to produce gases, acetylene and methane. These reactions are shown with water in Equations 21 and 22.

These reactions will be considered undesirable side reactions. To determine if the solvents chosen react with carbides similarly, the solvent and a small amount carbide will be placed in sealed containers. The amount of carbide to be used can be determined by assuming total conversion to gas. Then, for a container of given volume the maximum pressure produced can be determined. The amount of carbide to be used will be less than the amount that could produce a pressure exceeding the maximum pressure rating of the container. (This assumes the gas is insoluble in the solvent. If this assumption is invalid, a lower pressure will be reached during the experiment and the experiment will still be safe.) If the carbide is shown to degrade in the solvent alone, that solvent is incompatible with that carbide. (Note: the mechanism for reaction is

similar in both carbides, so if a solvent is incompatible with one carbide, it is likely incompatible with the other.) Signs of degradation will be apparent before opening the container. Carbides react in this fashion to produce their respective hydroxides. The hydroxides are fine, white powders, whereas the carbides are not.

(3) Next, standard solubility tests will be done with all compatible solvents and all selected salts. Solubility of most of the salts can be found in literature. Because of the ease with which these tests can be done, the solubility of compatible solvents and salts will be determined experimentally. A given volume of solvent is measured, and salt is weighed and added until it no longer dissolves.

(4) Experiments will be done to see if the desired reactions can occur in the solvent phase. These will consist of placing the solvent, salt, and carbide in a sealed container, and allowing it to sit for a period of time (the duration of which is unknowable at present). If visible signs of reaction appear, the products would be purified and analyzed. Visible signs of reaction are expected to be the presence of metal, the presence of carbon (black material, most likely), and possibly a change in color. (Cupric and ferric chloride have a color when dissolved in most solvents. As the salt is consumed, the intensity of the color would diminish.)

If the preliminary experiments show that the reactions do indeed occur in the solvent phase, then future experiments will be done to attempt to control the reactions via this route.

3.3. Task 3 Analysis of Products

Carbon can be analyzed using multiple techniques. Virtually any analytic technique that would be needed is available for use. These include scanning-electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Raman spectroscopy, and cross-polarized optical microscopy.

SEM can be used to characterize the morphology of samples produced. The SEM available is a Hitachi S-4700 equipped with an EDAX EDS X-ray analyzer. The samples to be produced are ideal for SEM analysis: they are conductive, (or at least semi-conductive) solid, and homogeneous (small samples are representative). Different allotropes of carbon look very different at the micro-scale. EDS can determine what elements are present and in what relative amounts. This will be useful in verifying that the samples are clean (pure carbon).

XRD can be used to determine the structures of any crystalline compounds. The XRD available for use is a PANalytical X'Pert Pro XRD. The instrument is ideal for powder samples, and has a very high throughput. Using XRD, graphite and graphite can be differentiated, although not conclusively. Some forms of graphite have peaks that overlap some forms of diamond.

Raman spectroscopy determines low-frequency modes in a crystalline molecule. The Raman device available is a Renishaw InVia Raman Microscope. The device available is used for analyzing individual crystals, and cannot measure bulk properties. Raman

spectroscopy is a definitive test for carbon allotropes. It can positively differentiate diamond, graphite, and graphene.

3.4. Task 4 Evaluation of Parameters on Carbon Produced

There is no reason to expect that the solution reactions will not work. Essentially the ionization of the metallic halide salts would increase mass transfer so the reaction should take place faster than in the molten salts. The potential of the metallic cation reduction reaction can be controlled by concentration as per the Nernst Equation so by using a range of metallic cations a scan of the potential effects on the products of carbide oxidation can be determined. The clean-up procedure as described earlier will be abbreviated since the salt products should already be in solution. The same analytical procedures will be used to characterize the products.

3.5. Task 5 Design of a System to Control Reaction

If the reactions can take place in a solvent rather than only in molten salts, then it may be possible to isolate both half reactions. This will only be possible if the salt like carbides are electrical conductors. Examination of the carbides in the SEM did not indicate charging so it is expected that they are somewhat electrically conductive. If that is true then there can be two separate chambers: one containing a metallic salt solution in a non-carbide reactive solvent with the base metal immersed in the solution, the second chamber would contain a calcium chloride solution dissolved in the same non-carbide reactive solvent. Calcium carbide contained in a non-reactive, conductive basket would be immersed in this chamber. The two chambers would be connected by a salt bridge so ions could flow between both chambers. Subsequently a wire would be

attached to that part of the base metal sticking out of the solution and the other end of the wire would be attached a wire from the basket containing the carbide sticking out of the solution. The experimental setup is shown in Figure 1.

Figure 1 – 2-cell Experimental Setup

This is essentially a galvanic battery. Electrons would travel from the carbide electrode to the metallic electrode. Metallic cations in solution would travel to the metallic electrode where they would pick up electrons and be reduced to elemental metal. Simultaneously the carbide would be oxidized to elemental carbon. In order to maintain charge balance, the anions, chloride ions from the metallic salt solution, would travel through the salt bridge to the carbide immersed in solution where they would unite with the calcium cations and produce a calcium chloride salt. The reduction potential of

the non-carbide cell can be changed by changing the metal and/or changing the concentration of ions in solution. The system would only produce the calcium halide salt and carbon in that chamber so clean up and analysis of products would be very easy. (There would be no metal in the carbide cell.)

4. Results and Conclusions for Each Task

4.1. Task 1 – Analytical Techniques

4.1.1. SEM-EDS

In short, an SEM (scanning-electron microscope) works by scanning a highly-focused electron beam over a sample, and counting how many electrons strike a detector at each point on the sample. These counts are used to generate an image. More electrons striking a detector means a brighter spot on the image. The image generated is, more or less, like a photograph of the sample. Unusual electronic behavior in a sample can cause irregularities. For a comparison of morphology via SEM analysis, it is helpful to look at known samples.

EDS (energy-dispersive X-ray spectroscopy) is almost always accompanied by an SEM. This is because an electron beam is required. The electron beam, rather than bouncing off the sample and striking a detector, excites an atom in the sample. The electron is placed in a higher-than-ground state. As the electron falls back down to its ground state, an X-ray is emitted. EDS uses an X-ray detector to look at the energy of these X-rays. The energy of the X-ray can be used to determine the elemental composition of a sample. Note that this gives no information on bonding. Only atomic composition can be determined.

The merits of SEM-EDS are:

1. It is a quick technique, requiring only minutes of sample preparation, and minutes of analysis. All samples of interest are either conductive or semi-conductive, meaning no metallic coating is required.
2. It provides compelling evidence for what allotrope has been produced by observing morphology. Planar crystals (graphite) are very different in appearance from octahedral crystals (diamond), and both are very different from non-crystalline carbon (amorphous carbon).
3. Elemental analysis (EDS) can verify the efficacy of cleaning techniques, and identify unexpected contaminants found in reactants.

Figure 2 – A sample with a high amorphous content, as measured by XRD later. This sample showed no peaks on XRD, an indication that it is amorphous. “10.0 kV” refers to voltage energy of the electron beam. It is the potential difference between the beam source and the sample. “11.9mm” is the working distance. This means that anything that is a distance of 11.9mm from the electron beam will be in perfect focus. “500” is the magnification. “100um” means that the entire scale bar is 100 microns in length. Each tick mark is 10 microns.

Figure 3 – A diamond crystal. Note the stair-steps, and angular nature of the edges.

Figure 4 – A diamond crystal. Note the concentric rings coming from a fracture mark. Fracture marks are another indicator of crystal structure.

Fracture marks as shown in Figure 4 are known as conchoidal fracture marks. By combining the observation of such features with EDS, a compelling case for what allotrope is shown can be made. EDS (not shown) indicated that this crystal is carbon. Diamond is the only known allotrope of carbon to have conchoidal fracture marks. While this makes a strong case, it is not proof positive that the crystals are diamond. For proof positive, Raman spectroscopy (discussed later) must be done. Throughout this research, the primary analytical tool used was the SEM-EDS.

Figure 5 – A graphite crystal.

Graphite, as shown in Figure 5, forms 2D sheets that are loosely bound in the third dimension. This image is at an angle to the edge.

An important, somewhat subtle fact to keep in mind when looking at EDS spectra is that carbon does not have a strong response to EDS. That is, in equal amounts (atomically), carbon peaks will be small. This can be shown by analysis of silicon carbide.

Figure 6 – EDS Spectrum of Silicon Carbide Wafer. The horizontal axis represents the energy of collected X-rays in keV. A given element has one or more peaks at fixed energies. Heavier elements (higher Z) have higher energies. The vertical axis is simply counts.

Note how the silicon peak is far larger than the carbon peak, even though silicon carbide is 1:1 in stoichiometry. This is not a result of difference in molecular weight, either. Even by mass, silicon carbide is 30% carbon. The relative shortness of the peak is a result of carbon's electronic structure and small cross-section. The effect of this phenomenon on the analysis of carbon containing samples is that seemingly large peaks for byproducts could compose only a small fraction of the makeup of a sample. In short, if carbon is the largest peak, the sample is mostly carbon.

Most EDS software packages are equipped with routines that can approximate quantitative analysis. These routines assume a flat, polished surface. For the spectrum shown in Figure 6, that assumption is valid. The wafer is atomically flat. And indeed, quantitative analysis shows the samples as being 50% silicon and 50% carbon (atomically). However, samples generated via molten-salt reactions are coarse powders

containing crystals and amorphous content with high surface area, so quantitative analysis from EDS spectra will have inherently high error. That being the case, they can provide order of magnitude accuracy. All samples that were subjected to the proposed cleaning techniques have shown a carbon content above 95%, by weight.

4.1.2. XRD

XRD analysis is used to determine crystal structures. XRD is divided into two main categories: powder and single crystal. For the purposes of this research, powder XRD will be used. XRDs work by irradiating a sample with focused X-rays at different angles of incident and observing how many X-rays are diffracted at each angle. Based on this information, computer programs can determine what crystal structures are present. By comparing that information to a database, a list of likely candidates can be generated.

The merits of XRD are:

1. It is a bulk technique.
2. It provides direct evidence of the allotrope of carbon.
3. It is automated. The available XRD has a 45 sample auto-sampler.

Raw XRD data is nearly impossible to interpret by inspection:

Figure 7 – XRD Pattern for 4.2.3. Molten Salt Experiment 3 – CaC_2 and ZnCl_2 . Different XRDs can have different configurations. The Panalytical X’Pert Pro that was used has a “Bragg-Brentano” configuration. The X-ray source is swept at an angle (θ) to the sample. The detector is swept at two times that angle (2θ). 2θ is the horizontal axis. The count of X-rays measured is the vertical axis.

Software reduces background influences and accounts for minor sample preparation imperfections. Peaks are identified, and a list of candidates is presented, along with a score representing how likely the candidate is. Note that peak height is in no way related to quantity, but rather crystal quality and crystal size. A single, perfect crystal of one compound in a sample that is primarily another will show very high and sharp peaks for the perfect crystal. Additionally, amorphous compounds will show no peaks at all. (This fact is exploited by using glass substrates, since they will not alter the XRD pattern at all.) XRD analysis of powders generated during this research were often inconclusive, as dozens or even hundreds of candidates are usually suggested by the software.

Because of this, XRD was much less useful for this research than was hoped. Using EDS results, potential candidates can be reduced. That is, if a sample is known to contain only carbon, oxygen, tin, chlorine, and iron, the list of candidates can be trimmed. Results from XRD analysis are summarized in Table 3.

Table 3 – XRD Results

Reaction	XRD Identified Candidates
$CaC_2 + ZnCl_2 \rightarrow 2C + Zn + CaCl_2$	C (two diamond patterns and graphite), Fe_2O_3 , CaOH
$CaC_2 + SnCl_2 \rightarrow 2C + Sn + CaCl_2$	C (diamond and graphite), Fe_2O_3 , Sn, SnO, SnO_2 , KOH
$Al_4C_3 + 6SnCl_2 \rightarrow 3C + 6Sn + 4AlCl_3$	C (diamond and graphite), Al_2O_3 , Sn, SnO, SnO_2 , KOH

The only new information gained from this analysis was the presence of alumina (Al_2O_3) in the aluminum carbide sample. This is thought to be from a contaminant in the production of aluminum carbide. Alumina is incredibly inert. Because of this, any technique that would remove alumina would destroy or alter any carbon. Since aluminum didn't show up in appreciable amounts in EDS spectra, it is most likely in trace quantities, and will be ignored.

4.1.3. Raman Spectroscopy

Raman spectroscopy uses a monochromatic laser to excite a sample from its ground state. The excited molecule can then fall back to its ground state (Rayleigh scattering) or to either a higher or lower energy state (Raman scattering). If it falls to a higher or lower energy state, the emitted photon will have a different energy. Raman spectroscopy measures how much Raman scattering occurs at different energy levels. The energy is often reported as wavenumbers in cm^{-1} . The available Raman spectrometer uses a green

laser and is a micro Raman spectrometer. The beam goes through a microscope, excites the sample, and the shifted photons are collected back through the microscope.

Because of this, only small areas can be analyzed at one time.

The importance of Raman spectroscopy for this research was differentiating different allotropes of carbon. Graphite, diamond, and graphene all have different Raman spectra. Diamond has a peak 1333 cm^{-1} . Graphite has a primary peak at 1580 cm^{-1} and smaller peak at 2720 cm^{-1} . Graphene has peaks at the same locations as graphite, but the primary peak is at 2720 cm^{-1} and the smaller peak is at 1580 cm^{-1} . In practice, diamond and graphite often have defects. This shows up in Raman spectra as diamonds having graphitic peaks, and graphite having a diamond-like peak.

Raman analysis of the products of all molten-salt reactions showed primarily amorphous material, with graphitic in some locations. Using Raman spectroscopy, all samples appeared to be nearly identical.

Figure 8 – Typical Raman spectrum of molten salt sample. Two broad peaks around 1500 cm⁻¹ are indicative of carbon.

Broad peaks indicate low quality crystals. In this case, the peaks are so broad that they run into each other. This is indicative of amorphous carbon.

Figure 9 – Another Raman spectrum typical of all molten salt reactions. This indicates graphite.

Figure 9 shows more graphitic nature. The low energy peak ($\sim 100\text{ cm}^{-1}$) is an error on the instrument, but does not affect the other readings. The small, sharp peak around 1400 cm^{-1} on the right side of the 1333 cm^{-1} peak is the result of a cosmic ray. The diamond peak at 1333 cm^{-1} resulted from a defect in the graphitic structure. Diamond can also have a secondary peak at 2470 cm^{-1} . This can be seen as the smallest peak in this spectrum.

When looking at an SEM image, it can be tempting to want a Raman spectrum for a particular crystal. However, to identify a crystal for analysis with Raman spectroscopy, it must be located in an optical microscope.

Figure 10 – Optical Microscopy from Raman microscope

It can be very difficult to determine if the crystal shown in an optical microscope is the same as the crystal seen in an SEM image. Additionally, the crystals are very small in absolute terms (10's of μm) and thus individual crystals cannot be isolated mechanically.

While Raman spectra for molten-salt reactions were all similar, it proved to be a very useful technique for solvent-phase reactions. The analysis of these products is discussed in Task 5.

4.2. Task 2 – Selection of Carbides and Metallic Halide Salt

The purpose of Task 2 is to make the selection of the most suitable carbide and metal halides to be used based on commercial availability, reactivity, and physical properties of the materials.

The selection of potential salts can be done by analysis of physical properties. The properties of interest are: melting point of the salt, reduction potential of the cation, electronegativity of the anion, and the solubility in potential solvents (This will be discussed in Task 2 – Selection of Potential Solvents.). For some salts, significant safety considerations could override use as a reactant.

As described in Reaction of Metal Carbides, Dissertation Research Proposal, the salts that meet the requirement of low melting point (below 500°C) and low reduction potential (above -1 V) are stannous chloride, zinc chloride, and ferric chloride. These salts are all commodity chemicals and are available at analytical purity from numerous vendors.

The selection of carbides is limited both physically and practically. Covalent, complex, and interstitial carbides are, in most environments, non-reactive. In fact, covalent carbides are so inert, they are used as a refractory. However, the reactions of interest

are not typical. What is inert in one environment may react when exposed to different reagents and conditions.

Two experiments were performed to evaluate the potential for covalent carbides to be used as the reducing agent in the reactions of interest. Powdered silicon carbide was chosen as the carbide. Both stannous fluoride and stannous chloride were tested as the metallic halide.

These salts were chosen because in preliminary reactions, calcium carbide and aluminum carbide both reacted with stannous fluoride and stannous chloride. These reactions are detailed in Reactions of Metal Carbides, Dissertation Research Proposal. In short, the carbides and salts were crushed, mixed, and heated to 50°C above the melting point of the salt. They were left at that temperature for 72 hours. Upon analysis of the products, elemental tin and carbon were found, indicating that the reaction had occurred. Although not shown, all experiments for Task 2 were done in triplicates. The following experimental apparatus was used for all molten salt experiments:

Figure 11 – Experimental apparatus used. Red indicates the heated fluidized bed. Blue indicates alkaline water to absorb corrosive gases. The sample is loaded into the black vessel. A vacuum is pulled. Any gas emitted by the reactor must first bubble through alkaline water.

4.2.1. Molten Salt Experiment 1 – SiC and ZnCl₂

An experiment was performed to determine if the following reaction occurs under mild reacting temperatures:

Materials

- 22.4 g powdered silicon carbide
- 152.6 g zinc chloride
- 800 g water
- 200 g sodium hydroxide

Equipment

- 200 mL tall-form borosilicate beaker
- Stainless steel flanged vessel
- Copper gasket
- Stainless steel tubing
- Fluidized bed electric heater
- House vacuum line
- Argon purged, dry glovebox

Procedure

The silicon carbide and zinc chloride were added to the tall-form beaker in the glovebox and stirred to combine. Both were available as fine powders, and needed no crushing. The masses were chosen to provide 100% stoichiometric excess zinc chloride, and so the total mass of solids would be 150 g. This mass equates to a volume slightly below 100 mL, half the capacity of the tall-form beaker. Additionally, this mass could produce 6.7 g of carbon, if the reaction goes to 100% completion. This would be a sufficient amount for any analysis needed.

The beaker was then placed in the stainless-steel vessel and sealed with a copper gasket and fitted with a hand-operated, Swagelok valve. The valve was closed, and the vessel was removed from the glovebox. It was then attached to the tubing above the fluidized bed electric heater. The tubing was connected to a bubbler assembly. Sodium hydroxide and water were placed in the bubbler flask. The flask was also connected to the house-vacuum line. The heater bed was set to 300°C, 10°C above the melting point of zinc chloride.

After reaching 300°C, the bed was raised up to submerge the reactor. The hand operated valve was opened. The house vacuum line was opened. The bed was left at this temperature for 72 hours. After 72 hours, the heater was turned off. The hand-operated valve was closed to prevent any backflow from the bubbler as the reactor cooled. The reactor was returned to the glovebox, where it was opened.

Safety

Silicon tetrachloride, a possible product and liquid at room temperature, is a gas at reaction conditions. To prevent a buildup of pressure caused by the formation of a gas, it was drawn out with a vacuum. The silicon tetrachloride would then react with water in the bubbler to form silica and hydrochloric acid in the bubbler. The acid would be neutralized by the sodium hydroxide. 5.0 moles of sodium hydroxide were more than sufficient to neutralize the 0.57 moles of silicon tetrachloride that could potentially be produced. (1 mole of SiCl_4 produces 4 moles of HCl .)

Results

Upon opening the reactor, it was immediately apparent that no reaction took place. The salt melted and settled below the silicon carbide. Silicon carbide, ground to the size available, has a slightly green color, which was observed before and after the reaction. SEM analysis provided no useful images, as all material was non-conductive.

Conclusions

Silicon carbide is likely unsuitable as a carbide. If it reacts at all with molten salts, it's likely that the temperature required is high enough to react any useful carbon products to amorphous carbon or graphite. To verify this, a more reactive salt must be used. This was not done originally because more reactive salts (fluorides) are more hazardous.

4.2.2. Molten Salt Experiment 2 – SiC and SnF_2

An experiment was performed to determine if the following reaction occurs:

Materials

- 22.7 g powdered silicon carbide

- 177.3 g stannous fluoride
- 800 g water
- 200 g sodium hydroxide

Equipment

- 200 mL tall-form borosilicate beaker
- Stainless steel flanged vessel
- Copper gasket
- Stainless steel tubing
- Fluidized bed electric heater
- House vacuum line
- Argon purged, dry glovebox

Procedure

The silicon carbide and stannous fluoride were added to the tall-form beaker in the glovebox and stirred to combine. Both were available as fine powders, and needed no crushing. The masses were chosen to provide 100% stoichiometric excess stannous fluoride, and so the total mass of solids would be 200 g. This mass equates to a volume of approximately 100 mL, below the half the capacity of the tall-form beaker. Higher masses could be used for this experiment as stannous fluoride packs more densely than zinc chloride. This mass of reactant could produce 6.8 g of carbon, if the reaction goes to 100% completion. This would be a sufficient amount for any analysis needed.

The beaker was then placed in the stainless-steel vessel and sealed with a copper gasket and fitted with a hand-operated, Swagelok valve. The valve was closed, and the vessel was removed from the glovebox. It was then attached to the tubing above the fluidized bed electric heater. The tubing was connected to a bubbler assembly. Sodium hydroxide and water were placed in the bubbler flask. The flask was also connected to the house-

vacuum line. The heater bed was set to 265°C, 10°C above the melting point of stannous fluoride.

After reaching 265°C, the bed was raised up to submerge the reactor. The hand operated valve was opened. The house vacuum line was opened. The bed was left at this temperature for 72 hours. After 72 hours, the heater was turned off. The hand-operated valve was closed to prevent any backflow from the bubbler as the reactor cooled. The reactor was returned to the glovebox, where it was opened.

Safety

The caustic water in the bubbler would absorb and neutralize any silicon tetrafluoride produced. The silicon tetrafluoride would react to form silicic acid and hydrofluoric acid. The acids would be neutralized by the sodium hydroxide. 5.0 moles of sodium hydroxide were more than sufficient to neutralize the 0.57 moles of silicon tetrafluoride that could potentially be produced. (1 mole of SiF_4 can produce 4 moles of HF.) Silicon tetrafluoride is a gas at room temperature, unlike silicon tetrachloride. So absorption into water was essential.

Results

Upon opening the reactor, it was immediately apparent that no reaction took place. The salt melted and settled below the silicon carbide. Silicon carbide, ground to the size available, has a slightly green color, which was observed before and after the reaction. SEM analysis provided no useful images, as all material was non-conductive.

Conclusions

Silicon carbide is unsuitable as a carbide for these experiments. Stannous fluoride should be the most reactive salt available, as fluorine is the most electronegative element and tin is easily reduced. If silicon carbide will not react with stannous fluoride, it will probably not react with any salt at any temperature that would provide useful carbon material. This implies that covalent carbides, which are inert under most conditions, are inert under conditions of interest to this research.

Since covalent carbides are not reactive, the search for potential carbides was restricted to salt-like (ionic) carbides. Availability turned out to be the limiting property in salt-like carbide use. Essentially two ionic carbides are produced commercially: calcium carbide and aluminum carbide. Calcium carbide is used industrially to produce acetylene via reaction with water. Since it is used as a feedstock for a commodity chemical, it is inexpensive (\$0.04/g). It is produced from coke, and thus has impurities associated with coal: sulfur iron primarily from American coals. The iron content of German calcium carbide is considerable lower.

Aluminum carbide is commercially available, but has much more limited use. It is used to prevent creep in some alloys and as an abrasive. However, because it is reactive with water, the abrasive applications are very specialized. Because of this, aluminum carbide is much more expensive (\$5/g). It is produced from graphite rather than coke. Thus aluminum carbide that is available commercially is very pure.

The only other ionic carbide of interest is magnesium carbide. Magnesium forms two carbides, Mg_2C and Mg_2C_3 (magnesium sesquicarbide). Neither carbide has a commercial application. Because of this, it must be synthesized. Synthesis, purification, and verification of the product was deemed outside the scope of this research.

A series of experiments was performed to see if calcium carbide and aluminum carbide react with molten salts to produce carbon. The reactions were carried out $10^\circ C$ above the salt's melting point. The reactions were allowed to occur for 72 hours. Additionally, the samples were used to determine the efficacy of the proposed cleaning procedure.

The experiments are summarized in Table 4:

Table 4: Ionic carbide-molten salt reactions for Task 2

Reaction	Reaction T	Experiment #
$CaC_2 + ZnCl_2 \rightarrow 2C + Zn + CaCl_2$	$302^\circ C$	Experiment 3
$CaC_2 + SnCl_2 \rightarrow 2C + Sn + CaCl_2$	$257^\circ C$	Experiment 4
$3CaC_2 + 2FeCl_3 \rightarrow 6C + 2Fe + 3CaCl_2$	$316^\circ C$	Experiment 5
$Al_4C_3 + 6ZnCl_2 \rightarrow 3C + 6Zn + 4AlCl_3$	$302^\circ C$	Experiment 6
$Al_4C_3 + 6SnCl_2 \rightarrow 3C + 6Sn + 4AlCl_3$	$257^\circ C$	Experiment 7
$Al_4C_3 + 4FeCl_3 \rightarrow 3C + 4Fe + 4AlCl_3$	$316^\circ C$	Experiment 8

It should be noted that an important, somewhat hidden variable in the experiments is the mass of carbon produced. Because of varying molecular weights, for a given mass of feed, very different masses of carbon will be produced. This must be considered to ensure that a enough carbon is produced to be analyzed. XRD, for example, can require grams to form a disc for powder analysis. All reactions were carried out at 100% excess

salt to ensure all carbide would be consumed. Table 5 summarizes the masses involved in the reactions described in Table 4, assuming a basis of 100 g of carbide.

Table 5: Weight Percent Summary for Reactions per 100 g Carbide

Carbide	Salt	Salt (g)	Carbon (g)	Carbon (wt%)
CaC_2	$ZnCl_2$	425.3	37.4	7%
CaC_2	$SnCl_2$	591.6	37.4	5%
CaC_2	$FeCl_3$	337.4	112.3	26%
Al_4C_3	$ZnCl_2$	1136.3	25.0	2%
Al_4C_3	$SnCl_2$	1580.4	25.0	1%
Al_4C_3	$FeCl_3$	901.4	25.0	2%

4.2.3. Molten Salt Experiment 3 – CaC_2 and $ZnCl_2$

An experiment was performed to see if the following reaction occurs at 302°C:

Additionally, the material produced was subjected to the cleaning procedure described in 3. *Research Plan*.

Materials

- 38.1 g CaC_2
- 161.9 g $ZnCl_2$
- 100 mL conc. HCl
- Distilled water
- 100 mL methanol

Equipment

- 200 mL tall-form borosilicate beaker
- Stainless steel flanged vessel fitted with a valve
- Copper gasket
- Fluidized bed electric heater
- Argon purged, dry glovebox
- Borosilicate tray
- Fine, borosilicate glass fritted vacuum filtering assembly
- Magnetic stir bar
- Magnetic stir plate

Procedure

The calcium carbide and zinc chloride were added to the tall-form beaker in the glovebox and stirred to combine. Calcium carbide was available as coarse chunks, 1 to 5 cm across. It was ground in an argon-filled glovebox using a mortar and pestle. Zinc chloride was available as a fine powder. The masses were chosen to provide 100% stoichiometric excess zinc chloride, and so the total mass of solids would be 200 g. This mass equates to a volume of approximately 100 mL, below the half the capacity of the tall-form beaker. This mass of reactant could produce 14.2 g of carbon, if the reaction goes to 100% completion. This would be a sufficient amount for any analysis needed.

The beaker was then placed in the stainless steel vessel and sealed with a copper gasket and fitted with a hand-operated, Swagelok valve. The valve was closed, and the vessel was removed from the glovebox. It was then attached to the tubing above the fluidized bed electric heater. The tubing was connected to a bubbler assembly. The flask was also connected to the house-vacuum line. The heater bed was set to 302°C, 10°C above the melting point of zinc chloride.

After reaching 302°C, the bed was raised up to submerge the reactor. The hand operated valve was opened. The house vacuum line was opened. The bed was left at this temperature for 72 hours. After 72 hours, the heater was turned off. The hand-operated valve was closed to prevent any backflow from the bubbler as the reactor cooled.

The reactor was then opened in a fume hood. The 200 mL tall-form beaker was removed from the stainless steel vessel, and placed in a larger borosilicate tray to catch any potential overflow. The 14 M acid was diluted into the distilled water and added to the beaker. This was stirred periodically until the solid plug was free from the 200mL tall-form beaker. The plug was broken up by using a glass stirring rod until all solids were suspended in the acid. Fresh acid was added to the beaker, and it was placed on a stir plate overnight.

The suspension was then filtered on the glass-fritted filter using house vacuum. The retentate was washed using the remaining acid, then rinsed with distilled water. The retentate was washed with methanol to dry it.

Safety

Although calcium chloride is not volatile like the salts potentially produced in previous experiments, the same physical assembly (reactor, bubbler, etc.) was used for this experiment. At the very least, the vacuum line would prevent any pressure buildup caused by heating the argon left in the headspace of the reactor. It should be noted that the pressure could only increase to approximately 2 atm. at this temperature.

Upon addition of water or acid, any remaining calcium carbide will rapidly react via Equation (23 to produce acetylene gas. Because of this the cleaning procedure should be performed with small additions of water or acid at one time and it should be performed in a fume hood.

Results

Upon opening the reactor, it appeared as though a reaction had taken place. The contents had changed from an off-white mixture (crushed calcium carbide is grey and crushed zinc chloride is white) to a dark grey, solid plug. Upon addition of acid, the mixture foamed violently and released a noticeable amount of heat. The odor of acetylene was noticed. Because of that, acid had to be added very slowly.

It should be noted that the production of gas is from unreacted calcium carbide, and is not an indication that the reaction happened. Zinc metal will react similarly with acid (exothermic reaction with a production of gas) to produce zinc chloride and hydrogen gas, but this is impossible to differentiate from the formation of acetylene without gas analyzing equipment.

After gas producing reaction appeared to have completed, a suspension of fine, very dark black, shimmering particles in acid remained. The appearance was similar to glitter in blank ink. The particles would settle if the solution was allowed to rest. Once this was filtered and washed with methanol, an easily broken up black cake remained. The mass of the cake was approximately 6.4 g, indicating that the reaction went to approximately 45% completion. This cake was analyzed with SEM-EDS to determine if carbon was produced by the reaction. The powder was mixed to make it homogeneous, and a small sub-sample was placed on double-sided carbon tape for SEM-EDS analysis. An unexpected result was the appearance of magnetic beads and filings on the stir bar.

Figure 12 – SEM Micrograph of the products of 4.2.3. Molten Salt Experiment 3 – CaC_2 and ZnCl_2

Figure 13 – EDS Spectrum of **Error! Reference source not found.**, showing mostly carbon.
Note, a large carbon peak indicates a very high carbon concentration in EDS.

Other areas of the same sample showed similar composition. However, there were various morphologies found.

Figure 14 – Different morphology seen in this reaction. Elemental analysis shows this to be pure carbon. However, this particle appears to be smooth.

Figure 15 – Different morphology seen in this reaction. Again, pure carbon, but this appears more jagged.

Conclusions

The reaction appears to have occurred as expected. That is, no other hypothesized reaction would have produced carbon. During preliminary reactions with tin salts, immediate evidence that the reaction occurred was visible when beads of tin were found. Zinc, however, melts at 420°C, well above the maximum temperature of this experiment, so zinc would have remained as very small crystals, not spheres.

Different morphologies of carbon suggest that different allotropes of carbon could have been formed during the reaction. Zinc chloride and calcium carbide appear to be compatible reactants for this set of experiments, and the cleaning procedure was very effective. Notably, this is the first time that the carbide anion was reduced to elemental carbon at a temperature below 800°C.

The filings and beads found on the stirring rod were analyzed for elemental composition using EDS. Both filings and beads were found to be iron metal. It was determined that the iron contaminant came from calcium carbide.

4.2.4. Molten Salt Experiment 4 – CaC₂ and SnCl₂

An experiment was performed to see if the following reaction occurs at 257°C:

Additionally, the material produced was subjected to the cleaning procedure described in 3. *Research Plan*.

Materials

- 28.9 g CaC₂
- 171.1 g SnCl₂
- 100 mL conc. HCl
- 500 g KOH

- Distilled water
- 100 mL methanol

Equipment

- 200 mL tall-form borosilicate beaker
- Stainless steel flanged vessel fitted with a valve
- Copper gasket
- Fluidized bed electric heater
- Argon purged, dry glovebox
- Borosilicate tray
- Fine, borosilicate glass fritted vacuum filtering assembly
- Magnetic stir bar
- Magnetic stir plate

Procedure

The calcium carbide and stannous chloride were added to the tall-form beaker in the glovebox and stirred to combine. Calcium carbide was available as coarse chunks, 1 to 5 cm across. It was ground in an argon-filled glovebox using a mortar and pestle. Stannous chloride was available as a coarse powder (think kosher salt). It was ground to a fine powder in the same fashion as the calcium carbide. The masses were chosen to provide 100% stoichiometric excess stannous chloride, and so the total mass of solids would be 200 g. This mass equates to a volume of approximately 100 mL, below the half the capacity of the tall-form beaker. This mass of reactant could produce 10.8 g of carbon, if the reaction goes to 100% completion. This would be a sufficient amount for any analysis needed.

The beaker was then placed in the stainless steel vessel and sealed with a copper gasket and fitted with a hand-operated, Swagelok valve. The valve was closed, and the vessel was removed from the glovebox. It was then attached to the tubing above the fluidized

bed electric heater. The tubing was connected to a bubbler assembly. The flask was also connected to the house-vacuum line. The heater bed was set to 257°C, 10°C above the melting point of stannous chloride.

After reaching 257°C, the bed was raised up to submerge the reactor. The hand operated valve was opened. The house vacuum line was opened. The bed was left at this temperature for 72 hours. After 72 hours, the heater was turned off. The hand-operated valve was closed to prevent any backflow from the bubbler as the reactor cooled.

The reactor was then opened in a fume hood. The 200mL tall-form beaker was removed from the stainless-steel vessel, and placed in a larger borosilicate tray to catch any potential overflow. The distilled water and added to the beaker. This was stirred periodically until the solid plug was free from the 200 mL tall-form beaker. The plug was broken up by using a glass stirring rod until all solids were suspended in the water.

The suspension was then centrifuged. (SnO and SnO₂ form a gel-like substance with water, which makes filtration impossible.) The centrate was rinsed in distilled water and centrifuged again. Then, a hot, concentrated potassium hydroxide solution was made by the addition of water (97 g KOH/100 mL water at approximately 80°C). The centrate was added to the hot KOH solution, which was stirred and heated for approximately two hours. This was centrifuged, decanted, and a fresh KOH solution was added. This was stirred and heated for 2 hours then filtered. The retentate was then rinsed with dilute

acid to remove any remaining KOH and CaOH, then rinsed with methanol to dry the powder.

Safety

Although calcium chloride is not volatile like the salts potentially produced in previous experiments, the same physical assembly (reactor, bubbler, etc.) was used for this experiment. At the very least, the vacuum line would prevent any pressure buildup caused by heating the argon left in the headspace of the reactor. It should be noted that the pressure could only increase to approximately 2 atm. at this temperature.

Upon addition of water, any remaining calcium carbide will rapidly react via Equation (23 to produce acetylene gas. Because of this the cleaning procedure should be performed with small additions of water at a time and it should be performed in a fume hood.

Hot potassium hydroxide is extremely corrosive and irritating. With long exposure, it can etch glass, so the glass-fritted filters should be checked for integrity regularly. If water is added to hot KOH, it can cause violent boiling from the heat of solvation.

Results

Upon opening the reactor, it appeared as though a reaction had taken place. The contents had changed from an off-white mixture (crushed calcium carbide is grey and crushed stannous chloride is white) to a dark grey, solid plug. Upon addition of water, the mixture foamed violently and released a noticeable amount of heat. The odor of acetylene was noticed. Because of that, water had to be added very slowly.

It should be noted that the production of gas is from unreacted calcium carbide, and is not an indication that the reaction happened.

After the reaction producing acetylene appeared to have completed, a gray sludge-like material remained. Visible beads of tin metal could be found. This material would blind any filters. Once treated with KOH, gas was evolved, and the material turned black and shimmered, similar to previous experiments. Once it was black, the SnO and SnO₂ were mostly dissolved, so it could then be filtered. Once the filtrate was dried with methanol, it formed a very dark, very fine powder. The mass of this powder was approximately 4.3 g, indicating that the reaction went to approximately 40% completion. This powder was placed on double-sided carbon tape for SEM-EDS analysis.

Figure 16 – SEM Image of 4.2.4. Molten Salt Experiment 4, showing a fine powder with some larger pieces.

Figure 17 – EDS Spectrum of 4.2.4. Molten Salt Experiment 4, showing mostly pure carbon. Some potassium and tin made it through the cleaning procedure.

Figure 18 – SEM image showing different carbon morphologies. Some are fine particles; some are angular chunks.

Figure 19 – SEM image showing surface texture of large piece shown in Figure 18

A solid bead of metal found in the sample was large enough to be extracted using forceps. It was removed and analyzed for composition as well.

Figure 20 – Tin bead isolated from 4.2.4. Molten Salt Experiment 4 – CaC_2 and SnCl_2

Figure 21 – EDS spectrum of bead shown in Figure 20, showing that the bead is metallic tin.

Conclusions

The reaction appears to have occurred as expected. Tin beads were visible after the reaction and elemental carbon was produced. The cleaning procedure successfully removed most contaminants. It should be noted that peak height on an EDS spectrum is NOT proportional to composition. Some atoms have higher chances of emitting an X-ray, some have lower. Carbon specifically has a lower chance, so a high carbon peak means a very high carbon composition. The beads found were determined to be tin, providing further evidence that the reaction happened as predicted.

4.2.5. Molten Salt Experiment 5 – CaC_2 and FeCl_3

An experiment was performed to determine if the following reaction occurs at 316°C and to determine if the proposed cleaning procedure is effective:

Materials

- 45.7 g CaC_2
- 154.3 g FeCl_3

- 100 mL conc. HCl
- Distilled water
- 100 mL methanol

Equipment

- 200 mL tall-form borosilicate beaker
- Stainless steel flanged vessel fitted with a valve
- Copper gasket
- Fluidized bed electric heater
- Argon purged, dry glovebox
- Borosilicate tray
- Fine, borosilicate glass fritted vacuum filtering assembly
- Magnetic stir bar
- Magnetic stir plate

Procedure

The calcium carbide and ferric chloride were added to the tall-form beaker in the glovebox and stirred to combine. Calcium carbide was available as coarse chunks, 1 to 5 cm across. It was ground in an argon-filled glovebox using a mortar and pestle. Ferric chloride was available as a fine powder. The masses were chosen to provide 100% stoichiometric excess stannous chloride, and so the total mass of solids would be 200 g. This mass equates to a volume of approximately 100 mL, below the half the capacity of the tall-form beaker. This mass of reactant could produce 51.4 g of carbon, if the reaction goes to 100% completion. This would be a sufficient amount for any analysis needed. Note this reaction has the most favorable stoichiometry of the six proposed reactions.

The beaker was then placed in the stainless-steel vessel and sealed with a copper gasket and fitted with a hand-operated, Swagelok valve. The valve was closed, and the vessel was removed from the glovebox. It was then attached to the tubing above the fluidized

bed electric heater. The tubing was connected to a bubbler assembly. The flask was also connected to the house-vacuum line. The heater bed was set to 316°C, 10°C above the melting point of ferric chloride.

After reaching 316°C, the bed was raised up to submerge the reactor. The hand operated valve was opened. The house vacuum line was opened. The bed was left at this temperature for 72 hours. After 72 hours, the heater was turned off. The hand-operated valve was closed to prevent any backflow from the bubbler as the reactor cooled.

The reactor was then opened in a fume hood. The 200mL tall-form beaker was removed from the stainless steel vessel, and placed in a larger borosilicate tray to catch any potential overflow. The acid was diluted into the distilled water and added to the beaker. This was stirred periodically until the solid plug was free from the 200 mL tall-form beaker. The plug was broken up by using a glass stirring rod until all solids were suspended in the water. This was allowed to stir on the magnetic stir plate overnight.

After the acid treatment, the suspension was filtered on the glass-fritted filter. It was rinsed with more acid, then rinsed with distilled water. Finally, the filtrate was dried using methanol.

Safety

Although calcium chloride is not volatile like the salts potentially produced in previous experiments, the same physical assembly (reactor, bubbler, etc.) was used for this

experiment. At the very least, the vacuum line would prevent any pressure buildup caused by heating the argon left in the headspace of the reactor. It should be noted that the pressure could only increase to approximately 2 atm. at this temperature.

Upon addition of acid, any remaining calcium carbide will rapidly react via Equation (23 to produce acetylene gas. Because of this the cleaning procedure should be performed with small additions of water at a time and it should be performed in a fume hood.

Results

Upon opening the reactor, it was unclear if the reaction had taken place. The contents changed from a dark grey-green (crushed calcium carbide is grey and anhydrous ferric chloride is green-black) to a dark yellow, solid plug. Upon addition of water, the mixture foamed violently and released a noticeable amount of heat. The odor of acetylene was noticed. Because of that, water had to be added very slowly.

It should be noted that the production of gas is from unreacted calcium carbide, and is not an indication that the reaction happened.

After filtering, very little material remained on the glass filter. So little that it could not be analyzed.

Conclusions

Calcium carbide produced from coke has some leftover coke as a byproduct of production. A control experiment (described in the 7. Appendix) showed that the calcium carbide used in this experiment contains approximately 0.5 wt% unreacted coke. This corresponds to 0.2 g of carbon. It is difficult to extract masses that small from a glass-fritted filter to weigh and analyze. A portion of the cake sticks to the filter, and if

the cake is too small, the portion that sticks comprises the entire cake. It is possible that the solids that remained on the filter were entirely unreacted coke from the calcium carbide, which means that a reaction did not take place.

Possible reasons for this include that the reaction simply cannot happen at the selected temperature. This is unlikely, as the ferric ion, Fe^{3+} , is the most easily reduced ion of all three chosen. Another potential reason is less thermodynamic and more practical. Ferric chloride is extremely hygroscopic, far more hygroscopic than stannous chloride and even zinc chloride (which is used as a desiccant). It is possible that the ferric chloride absorbed enough moisture in the glovebox to form $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ferric chloride hexahydrate. The glovebox used had a moisture indicator, which showed 0% moisture. The indicator may be less selective for water than ferric chloride.

It is unclear what effect water complexed with the salt would have on the reaction. However, it is likely that the water would become decomplexed during a reaction. If that happens, free water would be present to react with calcium carbide. It should be noted that ferric chloride hexahydrate is yellow, which is consistent with the color of the observed products. Ferric chloride may be too difficult to handle to be practical in these reactions. There are no dryer environments available than the glovebox for this research. Ferric chloride could be used to desiccate the glovebox, but it is far too expensive to do that.

4.2.6. Molten Salt Experiment 6 – Al_4C_3 and ZnCl_2

An experiment was performed to determine if the following reaction occurs at 302°C

and to determine if the proposed cleaning procedure is effective:

Materials

- 16.2 g Al_4C_3
- 183.8 g ZnCl_2
- 100 mL conc. HCl
- Distilled water
- Calcium hydroxide
- 100 mL methanol

Equipment

- 200 mL tall-form borosilicate beaker
- Stainless steel flanged vessel fitted with a valve
- Copper gasket
- Fluidized bed electric heater
- Argon purged, dry glovebox
- Borosilicate tray
- Fine, borosilicate glass fritted vacuum filtering assembly
- Magnetic stir bar
- Magnetic stir plate

Procedure

The aluminum carbide and zinc chloride were added to the tall-form beaker in the glovebox and stirred to combine. Aluminum carbide was available as a fine powder, -325 mesh. The powders were added to the tall-form beaker and stirred in the glovebox. The masses were chosen to provide 100% stoichiometric excess stannous chloride, and so the total mass of solids would be 200 g. This mass equates to a volume of approximately 100 mL, below the half the capacity of the tall-form beaker. This mass of reactant could produce 4.0 g of carbon, if the reaction goes to 100% completion. This is considerably

less than previous reactions. If the reaction does not go to completion, there may not be enough carbon for XRD analysis.

The beaker was then placed in the stainless-steel vessel and sealed with a copper gasket and fitted with a hand-operated, Swagelok valve. The valve was closed, and the vessel was removed from the glovebox. It was then attached to the tubing above the fluidized bed electric heater. The tubing was connected to a bubbler assembly. The flask was also connected to the house-vacuum line. The heater bed was set to 302°C, 10°C above the melting point of zinc chloride.

After reaching 302°C, the bed was raised up to submerge the reactor. The hand operated valve was opened. The house vacuum line was opened. The bed was left at this temperature for 72 hours. After 72 hours, the heater was turned off. The hand-operated valve was closed to prevent any backflow from the bubbler as the reactor cooled.

The reactor was then opened in a fume hood. The 200mL tall-form beaker was removed from the stainless-steel vessel, and placed in a larger borosilicate tray to catch any potential overflow. The acid was diluted into the distilled water and added to the beaker. This was stirred periodically until the solid plug was free from the 200 mL tall-form beaker. The plug was broken up by using a glass stirring rod until all solids were suspended in the water. This was allowed to stir on the magnetic stir plate overnight.

After the acid treatment, the suspension was filtered on the glass-fritted filter. It was rinsed with more acid, then rinsed with distilled water. Finally, the filtrate was dried using methanol.

Safety

Aluminum chloride has a very high vapor (>10 atm.) pressure at the temperature this experiment is operated. Because of this, a vacuum was drawn to remove any aluminum chloride formed. Aluminum chloride complexes with water to form aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$. Aluminum chloride hexahydrate decomposes to form hydrochloric acid and aluminum hydroxide via:

Because of this, calcium hydroxide was added to the water in the bubbler. This calcium hydroxide would neutralize and acid formed.

Upon the addition of water or acid, aluminum carbide will release methane gas via Equation (24)Because of this, acid must be added slowly.

Results

Upon opening the reactor, it was appeared as though a reaction had taken place. The contents changed from a dark yellow-green (aluminum carbide is yellow-green; zinc chloride is white) to dark grey. Upon addition of water, the mixture foamed and released a noticeable amount of heat. There was no odor, meaning the gas was likely methane. After filtering, very little material remained on the glass filter.

Conclusions

Since very little solids remained on the filter, it is unlikely that the reaction took place as predicted. It is possible that any carbon formed was so fine that it passed through the filter. The filtrate was a dark color. However, there were no finer filters available, and centrifugation did not provide any separations. Aluminum carbide was shown in preliminary experiments to react with stannous fluoride. Fluorine is more electronegative than chlorine, so perhaps higher electronegativity is needed.

4.2.7. Molten Salt Experiment 7 – Al_4C_3 and SnCl_2

An experiment was performed to see if the following reaction occurs at 257°C :

Additionally, the material produced was subjected to the cleaning procedure described in Research Plan.

Materials

- 11.9 g Al_4C_3
- 188.1 g SnCl_2
- 100 mL conc. HCl
- 500 g KOH
- Distilled water
- 100 mL methanol

Equipment

- 200 mL tall-form borosilicate beaker
- Stainless steel flanged vessel fitted with a valve
- Copper gasket
- Fluidized bed electric heater
- Argon purged, dry glovebox
- Borosilicate tray
- Fine, borosilicate glass fritted vacuum filtering assembly
- Magnetic stir bar
- Magnetic stir plate

Procedure

The aluminum carbide and stannous chloride were added to the tall-form beaker in the glovebox and stirred to combine. Aluminum carbide was available a fine powder, -325 mesh. Stannous chloride was available as a coarse powder (think kosher salt). It was ground to a fine powder using a mortar and pestle in the glovebox. The masses were chosen to provide 100% stoichiometric excess stannous chloride, and so the total mass of solids would be 200 g. This mass equates to a volume of approximately 100 mL, below the half the capacity of the tall-form beaker. This mass of reactant could produce 2.8 g of carbon, if the reaction goes to 100% completion. This would be a sufficient amount for any analysis needed, except XRD.

The beaker was then placed in the stainless-steel vessel and sealed with a copper gasket and fitted with a hand-operated, Swagelok valve. The valve was closed, and the vessel was removed from the glovebox. It was then attached to the tubing above the fluidized bed electric heater. The tubing was connected to a bubbler assembly. The flask was also connected to the house-vacuum line. The heater bed was set to 257°C, 10°C above the melting point of stannous chloride.

After reaching 257°C, the bed was raised up to submerge the reactor. The hand operated valve was opened. The house vacuum line was opened. The bed was left at this temperature for 72 hours. After 72 hours, the heater was turned off. The hand-operated valve was closed to prevent any backflow from the bubbler as the reactor cooled.

The reactor was then opened in a fume hood. The 200 mL tall-form beaker was removed from the stainless steel vessel, and placed in a larger borosilicate tray to catch any potential overflow. The distilled water was added to the beaker. This was stirred periodically until the solid plug was free from the 200 mL tall-form beaker. The plug was broken up by using a glass stirring rod until all solids were suspended in the water.

The suspension was then centrifuged. (SnO and SnO_2 form a gel-like substance with water, which makes filtration impossible.) The centrate was rinsed in distilled water and centrifuged again. Then, a hot, concentrated potassium hydroxide solution was made by the addition of water (97 g KOH/100 mL water at approximately 80°C). The centrate was added to the hot KOH solution, which was stirred and heated for approximately two hours. This was centrifuged, decanted, and a fresh KOH solution was added. This was stirred and heated for 2 hours then filtered. The retentate was then rinsed with dilute acid to remove any remaining KOH and $\text{Al}(\text{OH})_3$, then rinsed with methanol to dry the powder.

Safety

Aluminum chloride has a very high vapor (>10 atm.) pressure at the temperature this experiment is operated. Because of this, a vacuum was drawn to remove any aluminum chloride formed. Aluminum chloride complexes with water to form aluminum chloride hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Aluminum chloride hexahydrate decomposes to form hydrochloric acid and aluminum hydroxide via Equation (31). Because of this, calcium hydroxide was added to the water in the bubbler. This calcium hydroxide would

neutralize any acid formed. Upon the addition of water or acid, aluminum carbide will release methane gas via Equation (24). Because of this, acid must be added slowly. Hot, concentrated KOH is extremely caustic, and irritating to any tissue. Addition of water to hot KOH can cause violent boiling because of the high heat of solvation. Because of this, KOH must be cooled before any water can be added, if it is needed. Additionally, KOH can etch glass. This can weaken glass-fritted filters.

Results

Upon opening the reactor, it appeared as though a reaction had taken place. The contents had changed from a dark yellow-green (aluminum carbide is dark yellow-green and crushed stannous chloride is white) to a dark grey, solid plug. Upon addition of water, the mixture foamed violently and released a noticeable amount of heat. No odor was noticed, indicating that the gas could be methane.

After the reaction producing methane appeared to have completed, a gray sludge-like material remained. Visible beads of tin metal could be found. This material would blind any available filters. Once treated with KOH, gas was evolved, and the material turned black and shimmered, similar to previous experiments. The SnO and SnO₂ were mostly dissolved, and the black residue could then be filtered. Once the filtrate was dried with methanol, it formed a very dark, very fine powder. The mass of this powder was approximately 2.1 g, indicating that the reaction went to approximately 70% completion. This powder was placed on double-sided carbon tape for SEM-EDS analysis.

Figure 22 – SEM image of 4.2.7. Molten Salt Experiment 7 – Al_4C_3 and SnCl_2 .

Figure 23 – EDS of portion shown in Figure 22, showing that the cleaning procedure was successful. Some potassium hydroxide remained.

The crystals from this reaction appear to be larger than from previous reactions.

Figure 24 – Zoomed out image. Note the consistently larger crystals.

Conclusions

The reaction appears to have occurred as expected. Tin beads were visible after the reaction and elemental carbon was produced. The cleaning procedure successfully removed most contaminants. Relatively large single crystals usually indicate that the formation of the crystals occurred slowly. Particularly of interest is the size of carbon crystals is larger than the initial size of aluminum carbide (325 mesh corresponds to a 44 um). This implied that the crystals can grow together.

4.2.8. Molten Salt Experiment 8 – Al_4C_3 and FeCl_3

An experiment was performed to determine if the following reaction occurs at 316°C and to determine if the proposed cleaning procedure is effective:

Materials

- 20.0 g Al_4C_3

- 180.0 g FeCl_3
- 100 mL conc. HCl
- Distilled water
- 100 mL methanol

Equipment

- 200 mL tall-form borosilicate beaker
- Stainless steel flanged vessel fitted with a valve
- Copper gasket
- Fluidized bed electric heater
- Argon purged, dry glovebox
- Borosilicate tray
- Fine, borosilicate glass fritted vacuum filtering assembly
- Magnetic stir bar
- Magnetic stir plate

Procedure

The aluminum carbide and ferric chloride were added to the tall-form beaker in the glovebox and stirred to combine. Aluminum carbide was available as a fine powder, -325 mesh. Ferric chloride was available as a fine powder. The masses were chosen to provide 100% stoichiometric excess ferric chloride, and so the total mass of solids would be 200 g. This mass equates to a volume of approximately 100 mL, below the half the capacity of the tall-form beaker. This mass of reactant could produce 5.0 g of carbon, if the reaction goes to 100% completion. This would be a sufficient amount for any analysis needed, except XRD.

The beaker was then placed in the stainless-steel vessel and sealed with a copper gasket and fitted with a hand-operated, Swagelok valve. The valve was closed, and the vessel was removed from the glovebox. It was then attached to the tubing above the fluidized bed electric heater. The tubing was connected to a bubbler assembly. The flask was also

connected to the house-vacuum line. The heater bed was set to 316°C, 10°C above the melting point of ferric chloride.

After reaching 316°C, the bed was raised up to submerge the reactor. The hand operated valve was opened. The house vacuum line was opened. The bed was left at this temperature for 72 hours. After 72 hours, the heater was turned off. The hand-operated valve was closed to prevent any backflow from the bubbler as the reactor cooled.

The reactor was then opened in a fume hood. The 200mL tall-form beaker was removed from the stainless-steel vessel, and placed in a larger borosilicate tray to catch any potential overflow. The 14 M acid was diluted into the distilled water and added to the beaker. This was stirred periodically until the solid plug was free from the 200 mL tall-form beaker. The plug was broken up by using a glass stirring rod until all solids were suspended in the water. This was allowed to stir on the magnetic stir plate overnight.

After the acid treatment, the suspension was filtered on the glass-fritted filter. It was rinsed with more acid, then rinsed with distilled water. Finally, the filtrate was dried using methanol.

Safety

Aluminum chloride has a very high vapor (>10 atm.) pressure at the temperature this experiment is operated. Because of this, a vacuum was drawn to remove any aluminum chloride formed. Aluminum chloride complexes with water to form aluminum chloride

hexahydrate, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. Aluminum chloride hexahydrate decomposes to form hydrochloric acid and aluminum hydroxide via Equation (31. Because of this, calcium hydroxide was added to the water in the bubbler. This calcium hydroxide would neutralize any acid formed. Upon the addition of water or acid, aluminum carbide will release methane gas via Equation (24). Because of this, acid must be added slowly. Hot, concentrated KOH is extremely caustic, and irritating to any tissue. Addition of water to hot KOH can cause violent boiling because of the high heat of solvation. Because of this, KOH must be cooled before any water can be added, if it is needed. Additionally, KOH can etch glass. This can weaken glass-fritted filters.

Results

Upon opening the reactor, it was unclear if the reaction had taken place. The contents changed from a dark grey-green (aluminum carbide is dark yellow-green and anhydrous ferric chloride is green-black) to a dark yellow, solid plug. Upon addition of water, the mixture foamed violently and released a noticeable amount of heat. No odor was noticed. Because of the release of potentially flammable gas and heat, water had to be added very slowly.

After filtering, very little material remained on the glass filter. So little that it could not be analyzed.

Conclusions

Again, ferric chloride showed no potential as a reactant. Possible reasons for this include that the reaction simply cannot happen at the selected temperature. This is unlikely, as the ferric ion, Fe^{3+} , is the most easily reduced ion of all three cations chosen. Another

potential reason is less thermodynamic and more practical. Ferric chloride is extremely hygroscopic, far more hygroscopic than stannous chloride and even zinc chloride (which is used as a desiccant). It is possible that the ferric chloride absorbed enough moisture in the glovebox to form $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ferric chloride hexahydrate. The glovebox used had a moisture indicator, which showed 0% moisture. The indicator may be less selective for water than ferric chloride. This means that ferric chloride could absorb moisture from an atmosphere that the indicator shows as being completely dry.

It is unclear what effect water complexed with the cation would have on the reaction. However, it is likely that the water would become decomplexed during a reaction. If that happens, free water would be present to react with aluminum carbide. It should be noted that ferric chloride hexahydrate is yellow, which is consistent with the color of the observed products. Ferric chloride may be too difficult to handle to be practical in these reactions. There are no dryer environments available than the glovebox for this research. Ferric chloride could be used to desiccate the glovebox, but it is far too expensive to do that.

4.2.9. Summary of Task 2 Conclusions

Based on molten salt experiments, it has been determined which reactions take place.

Table 6 – Results Summary from Task 1

Reaction	Experiment #	Results
$SiC + 2ZnCl_2 \rightarrow SiCl_4 + C + 2Zn$	Experiment 1	No reaction
$SiC + 2SnF_2 \rightarrow SiF_4 + C + 2Sn$	Experiment 2	No reaction
$CaC_2 + ZnCl_2 \rightarrow 2C + Zn + CaCl_2$	Experiment 3	Reaction
$CaC_2 + SnCl_2 \rightarrow 2C + Sn + CaCl_2$	Experiment 4	Reaction
$3CaC_2 + 2FeCl_3 \rightarrow 6C + 2Fe + 3CaCl_2$	Experiment 5	No reaction
$Al_4C_3 + 6ZnCl_2 \rightarrow 3C + 6Zn + 4AlCl_3$	Experiment 6	No reaction
$Al_4C_3 + 6SnCl_2 \rightarrow 3C + 6Sn + 4AlCl_3$	Experiment 7	Reaction
$Al_4C_3 + 4FeCl_3 \rightarrow 3C + 4Fe + 4AlCl_3$	Experiment 8	No reaction

Calcium carbide appears to be more reactive than aluminum carbide. Ferric chloride is either unreactive or too hygroscopic to be of practical use (the latter being more likely). Stannous chloride appears to be the most reactive salt.

Varying morphologies were present in all reactions. There appeared to be amorphous, graphitic, and diamond-like crystals. Aluminum carbide reacted with stannous chloride to produce large crystals (larger than the initial aluminum carbide crystals). If these crystals are diamond, this could be very important, as it would provide a mild, liquid-phase route to synthetic diamonds. Evidence seems to indicate that the crystals grow together, so the diamonds could potentially be grown arbitrarily large.

Based on the results of Task 2, the research was limited to the analysis of the three reactions which were shown to occur: Experiments 3, 4, and 7. It should be noted that all reactions were run in triplicates. Experiment 5 was run six times. None of these six experiments produced carbon. (Experiments 6 and 8 were not run six times because of

the high cost of aluminum carbide. However, none of the triplicates for these experiments produced a measurable amount of carbon.)

4.3. Task 3 – Selection of Potential Solvents

The purpose of Task 3 is to determine if these reactions can be accomplished in media other than molten salts. The three carbide-salt pairs that reacted successfully in Task 2 were tested to determine if they would react in a solvent-phase reaction. First compatible solvents had to be selected. These solvents had to be non-reactive with the carbide and the salt, compatible with all equipment involved, and have a high solubility with the salt. This was the focus of Task 3.

In addition to molten salt reactions, it is possible that carbides can react with metal halides in the solvent phase. To do this, solvents must be chosen carefully. The molten reactions can give hints as to what properties are necessary. Since the reactions are redox reactions, the solvent must be capable of dissolving ionic salts. Water may appear to be a good choice. However, all ionic carbides react with water. The reaction of calcium carbide with water occurs via Equation (23).

This is the primary industrial route for acetylene synthesis. The reaction occurs very quickly, and thus cannot be an acceptable side reaction for this research. The mechanism for reaction involves proton attack of the carbide anion and hydroxide attack on the calcium cation. Thus, solvents that are proton donating (acidic) are not suitable. (Making the solution basic does not solve the problem either, since hydroxide anions can also initiate the reaction.) Properties of interest (in order of importance) now

include: ionizing, non-protonating, and inexpensive. Alcohols were the first choice. As the length of the alcohol increases, the acidic strength of the alcohol decreases. Solubility of salts tends to decrease. The solubility is tested in further detail in later experiments.

4.3.1. Solvent Selection Experiment 1 – CH₃OH

An experiment was performed to determine the compatibility of methanol and ethanol with calcium carbide. The suspected reaction is:

Calcium methoxide is an insoluble solid at the conditions of the reaction (room temperature). Acetylene is a flammable gas. Because of this, caution was taken to minimize the amount of gas produced. The reaction had to be performed in a sealed container to prevent any contamination (Methanol will absorb moisture from the air. This moisture will then react with the calcium carbide, which would taint the results of the experiment.).

Materials

- ~1 g piece of calcium carbide (0.98 used in experiment)
- 100 mL dry methanol (Procedure for drying available in appendix)

Equipment

- 200 mL borosilicate bottle with plastic cap

Procedure

100 mL of methanol was poured into the bottle. The calcium carbide (uncrushed) was placed in the lid of the bottle. The lid was placed on the bottle, and the cap was tightened quickly. The bottle was observed over the course of a week. The mixture was

then filtered so any solids could be analyzed. The carbide was left uncrushed to minimize the exposed surface area. This would prevent the reaction from happening too quickly (before the lid could be sealed), and minimize reaction with atmospheric moisture. After one week, water can be added to any remaining solids to confirm that the solids are calcium carbide.

Safety

Since the acetylene will form as a gas in a sealed container, precautions had to be taken to ensure that the bottle would not explode and could be safely opened. 100 mL of headspace was left in the bottle after the addition of methanol. The volume of the carbide was assumed negligible. The mass of calcium carbide would produce, if the reaction goes to completion, 0.02 moles of acetylene. This amount of acetylene, combined with the air in the headspace, would produce 5 atmospheres of pressure. This assumes that acetylene will not appreciably dissolve in the alcohol. Acetylene is known to be highly soluble in acetone (acetylene tanks use acetone to store the gas). This suggests that it may be soluble in methanol. If it is soluble, this will lower the final pressure below 5 atm. 5 atm. is well within the strength of the container. (Normal two-liter soda bottles can hold over 10 atm.) Additionally, the cap is threaded. This would allow any potential pressure to be released slowly in a fume hood.

Results

The carbide did not appear to be reacting with the methanol immediately upon contact. No bubbles formed. When carbide and water are combined, the reaction is immediate and violent. Over the first 2 hours, a small amount of white precipitate appeared in the

bottom of the bottle. After 12 more hours, the amount of precipitate increased steadily. After 5 days, the original piece of carbide was gone. Only white precipitate and methanol remained. The bottle was taken to a hood, and slowly opened. A small amount of pressure had built up, and the solution bubbled (much like opening a bottle of carbonated beverage). Careful wafting of the effluent revealed the presence of acetylene (a distinct, garlic-like odor). Elemental analysis (EDS, not shown) revealed the solid to be a combination of calcium, oxygen, iron, and trace sulfur. Addition of water yielded no gas, indicating that no calcium carbide remained.

Conclusions

Methanol does react with calcium carbide, albeit much more slowly than does water.

The elemental analysis is consistent with what would be expected from calcium methoxide. Hydrogen does not have a peak on the EDS used (the beryllium window absorbs any peaks below beryllium). Iron and sulfur are known contaminants in calcium carbide.

Methanol is a readily available, inexpensive, easily recovered material. This would make it an ideal solvent. If the desired reaction (with a metal halide salt) happens much more quickly than the reaction with methanol, then it can still be used as a solvent for the reaction. At this stage, methanol is not eliminated as a potential solvent.

Continuing from methanol, the next logical solvent is ethanol. A similar experiment was performed to determine how reactive ethanol is with calcium carbide.

4.3.2. Solvent Selection Experiment 2 – CH₃CH₂OH

An experiment was performed to determine the stability of calcium carbide in ethanol.

Specifically, does the following reaction happen, and if so, how quickly:

Materials

- ~1 g piece of calcium carbide (0.98 used in experiment)
- 100 mL anhydrous denatured ethanol (Procedure for drying available in appendix)

Equipment

- 1 x 200 mL borosilicate bottle with plastic cap

Procedure

100 mL of ethanol was poured into the bottle. (Note, the denaturing agents are purposefully difficult to remove. However, they are present in trace amounts, and thus deemed negligible.) The calcium carbide (uncrushed) was placed in the lid of the bottle. The lid was placed on the bottle, and the cap was tightened quickly. The bottle was observed over the course of a week. The mixture was then filtered so any solids could be analyzed. The carbide was left uncrushed to minimize the exposed surface area. This would prevent the reaction from happening too quickly (before the lid could be sealed), and minimize reaction with atmospheric moisture. After one week, water can be added to any remaining solids to confirm that the solids are calcium carbide.

Safety

Since the acetylene will form as a gas in a sealed container, precautions had to be taken to ensure that the bottle would not explode and could be safely opened. 100 mL of headspace was left in the bottle after the addition of ethanol. The volume of the carbide was assumed negligible. The mass of calcium carbide would produce, if the reaction

goes to completion, 0.02 moles of acetylene. This amount of acetylene, combined with the air in the headspace, would produce 5 atmospheres of pressure. This assumes that acetylene will not appreciably dissolve in the alcohol. Acetylene is known to be highly soluble in acetone (acetylene tanks use acetone to store the gas). This suggests that it may be soluble in ethanol. If it is soluble, this will lower the final pressure below 5 atm. 5 atm. is well within the strength of the container. (Normal two-liter soda bottles can hold over 10 atm.) Additionally, the cap is threaded. This would allow any potential pressure to be released slowly in a fume hood.

Results

After 7 days of exposure, the calcium carbide showed no visible signs of degradation. A very small amount of white powder was observed in the bottom of the container. This powder was too small to recover via filtration or centrifugation. No gas was released upon opening the bottle. Addition of water onto the remaining solids did yield acetylene, indicating that the remaining solid piece is indeed calcium carbide.

Conclusions

Ethanol does not apparently react with calcium carbide in a timescale of interest. The small white powder could be from trace methanol in the ethanol reacting with the calcium carbide. Ethanol can also pull moisture from the air. The white powder could then be calcium hydroxide. However, even if all of the calcium carbide reacted with water, the amount of calcium hydroxide produced would dissolve in the water (it is below the solubility limit). Because of this, ethanol is a strong candidate for a solvent.

4.3.3. Solvent Selection – THF, NMP, and Acetonitrile

Tetrahydrofuran (THF), n-methyl-2-pyrrolidone (NMP), and acetonitrile have severe reactions with many polymers. Specifically, they dissolve the gloves used in the available glovebox. Acetonitrile also dissolves the polymer that the window and exchange chamber are made of. Because of this, they cannot safely be loaded into the available glovebox. This means there is no safe way to load these reactions without exposing calcium carbide to moisture. Additionally, future experiments depend on the compatibility of solvents with polymers. NMP specifically is very difficult to recover via distillation because of its very high boiling point. Because of these reasons, THF, NMP, and acetonitrile have been removed as solvent candidates.

4.3.4. Solvent Selection Experiment 3 – Salt Solubility Tests

An experiment was conducted to determine if stannous chloride and zinc chloride are soluble in methanol and ethanol. (This information is available in literature, but with conflicting information.)

Materials

- 150 g ZnCl_2
- 150 g SnCl_2
- 200 mL CH_3OH
- 200 mL anhydrous, denatured $\text{CH}_3\text{CH}_2\text{OH}$

Equipment

- 4 x 200 mL borosilicate bottle with plastic cap
- Argon purged glovebox

Procedure

All materials and equipment were loaded into the glovebox. 100 mL of methanol was added to each of two of the bottles. 100 mL of ethanol was added to each of two bottles. 10 g of ZnCl_2 was added to one bottle with methanol, and one bottle of ethanol.

10 g of SnCl_2 was added to the other bottle of methanol, and the other bottle of ethanol. This is summarized in Table 7.

Table 7 – Summary of 4.3.4. Solvent Selection Experiment 3 – Salt Solubility Tests

Salt	Solvent	Bottle #
SnCl_2	Methanol	1
SnCl_2	Ethanol	2
ZnCl_2	Methanol	3
ZnCl_2	Ethanol	4

The bottles were sealed, and shaken until the salt disappeared. The bottles were opened and the process was repeated until no more salt would dissolve.

Safety

Since everything will be handled in the glovebox, there are few safety concerns. A surprising concern was the high heat of solvation in all soluble salt-solvent pairs. Because of this, salts must be added slowly, and the lids must be opened periodically to prevent a buildup of pressure.

Results

Both salts were found to be readily soluble in both solvents. Both salts were more soluble in methanol, over 50 g per 100 mL of solvent. Zinc chloride solubility in ethanol was found to be approximately 25 g per 100 mL. Stannous chloride solubility in ethanol was found to be approximately 15 g per 100 mL.

Conclusions

Based on this experiment, both salts were found to be sufficiently soluble in both solvents, and thus were used in later experiments.

Sealed Container Reactions

Based on results thus far, the potential solvents, carbides, and salts have been

determined:

Solvents

- Methanol
- Ethanol

Carbides

- Calcium carbide
- Aluminum carbide

Salts

- Stannous chloride
- Zinc chloride

4.3.5. Sealed Reaction Experiments

Based on this set, there were 8 possible experiments. To explore each of these, a series

of experiments were conducted to determine if the proposed reactions occur in a

solvent.

Materials

- 100 g SnCl_2
- 100 g ZnCl_2
- 900 mL methanol
- 400 mL dry ethanol
- 4 g CaC_2
- 4 g Al_4C_3
- 400 mL concentrated HCl
- 400 g KOH
- 400 mL distilled water

Equipment

- 8 x 200 mL borosilicate bottle with plastic cap
- Fine, borosilicate glass fritted vacuum filtering assembly
- 1 x strong permanent magnet

Procedure

25 g of salt was placed in each of four bottles. 100 mL of each solvent was placed in each of four bottles. 1 g of each carbide was placed in each of four bottles. This is summarized in Table 8:

Table 8 – Summary of Solvent-phase Reactions

Carbide	Salt	Solvent	Bottle #
CaC ₂	SnCl ₂	Methanol	1
CaC ₂	SnCl ₂	Ethanol	2
CaC ₂	ZnCl ₂	Methanol	3
CaC ₂	ZnCl ₂	Ethanol	4
Al ₄ C ₃	SnCl ₂	Methanol	5
Al ₄ C ₃	SnCl ₂	Ethanol	6
Al ₄ C ₃	ZnCl ₂	Methanol	7
Al ₄ C ₃	ZnCl ₂	Ethanol	8

The bottles were shaken periodically, and allowed to set for 72 hours. They were then opened slowly in a fume hood. The contents were filtered on the glass-fritted filter. Zinc reactions were washed with hydrochloric acid, then rinsed with distilled water, then dried with methanol. Tin-containing reactions were placed in beakers containing hot, concentrated potassium hydroxide, and allowed to stir overnight. The contents were then filtered, rinsed with hydrochloric acid, then rinsed with distilled water, then dried with methanol. If any solids remained, then the reaction must have happened. Carbon is the only material that can withstand the cleaning procedure.

Safety

Production of gas via degradation of the carbides by the solvents is the primary safety concern. However, it has already been shown that insufficient gas is produced to pose a

safety concern. The bottles should be opened slowly in a fume hood to release any gases slowly.

Results

Over the course of the reaction, it was apparent that reactions took place in 5 of the 8 bottles. Bottles 2, 6, and 8 showed no signs of change. It was unclear at this point what reaction(s) took place in the other bottles. The results are summarized in Table 9:

Table 9 – Summary of Sealed Container Reactions

Carbide	Salt	Solvent	Appearance before cleaning	Appearance after cleaning
CaC ₂	SnCl ₂	Methanol	White powder	No remaining solids*
CaC ₂	SnCl ₂	Ethanol	Unchanged piece of CaC ₂	No remaining solids*
CaC ₂	ZnCl ₂	Methanol	White powder with black pieces	Coarse, black powder
CaC ₂	ZnCl ₂	Ethanol	White powder with black pieces, unreacted CaC ₂	Coarse, black powder
Al ₄ C ₃	SnCl ₂	Methanol	White powder	No remaining solids
Al ₄ C ₃	SnCl ₂	Ethanol	Unchanged Al ₄ C ₃	No remaining solids
Al ₄ C ₃	ZnCl ₂	Methanol	White powder	No remaining solids
Al ₄ C ₃	ZnCl ₂	Ethanol	Unchanged Al ₄ C ₃	No remaining solids

* - Iron filings remained

Magnetic solids remained in Bottles 1 and 2. A strong permanent magnet was used to remove the magnetic particles. These filings are iron contaminants from calcium carbide production. Bottles 3 and 4 had non-magnetic solids that remained. No solids remained from bottles 5-8. In all cases, too little material was produced for analysis. Even if all of the carbides reacted to produce carbon, much less than 1 g of carbon would be produced.

Conclusions

It appears that aluminum carbide does NOT react in the solvent-phase. The exact reason for this is unclear, but it is likely a mass transfer issue. Aluminum carbide is a fine powder, so it has very high specific surface area. Higher surface area increases the rate of reaction with methanol. Ethanol probably reacts with both carbides, but too slowly to be noticed with calcium carbide. Since the rate of reaction with aluminum carbide is expected to be so much higher, ethanol may react with aluminum carbide quickly enough to consume all of it before any carbon can be produced.

Calcium carbide appears to react with zinc chloride in both methanol and ethanol. Methanol consumes a significant portion of both carbides in all cases; however, it appears that some calcium carbide reacts to produce carbon. Calcium carbide appears to not react with stannous chloride in solvent-phase reactions. There may be insufficient thermodynamic driving force to allow this reaction to happen (temperature is too low to provide the activation energy). This is unusual since tin has a lower reduction potential than zinc.

Based on this experiment, future experiments were focused on reactions between calcium carbide and zinc chloride in both ethanol and methanol.

4.3.6. Summary of Task 3 Conclusions

Methanol reacted with calcium carbide. However, the rate of reaction may be slow enough for it to still be a useful solvent. Additionally, methanol is inexpensive and easy to recover. (Methanol can be recovered via distillation alone.) Because of these reasons, methanol was used in later experiments.

Ethanol appears to be compatible with calcium carbide, and by extension compatible with aluminum carbide. On the timescale of the experiment, ethanol showed no signs of reaction. Additionally, ethanol is inexpensive, and somewhat easy to recover.

(Ethanol requires distillation and drying with molecular sieve, as it forms an azeotrope with water.) Because of these reasons, ethanol will be used in later tasks as a solvent.

Other solvents, NMP, THF, and acetonitrile, may be compatible with carbides, but they are incompatible with lab equipment that is available. Moreover, later tasks involve reactors that utilize polymer ion exchange membranes, which these solvents are incompatible with. Because of these reasons, NMP, THF, and acetonitrile will not be used in later tasks.

Zinc chloride is readily soluble in both methanol and ethanol. Stannous chloride is soluble only in ethanol. During the solvation of all pairs of solvent and salt, large amounts of heat were released.

Calcium carbide and zinc chloride is the only salt-carbide pair that reacts in the solvent phase. Methanol appears to consume significant portions of calcium carbide and consumes nearly all aluminum carbide much more quickly than the desired reaction rate.

4.4. Task 4 – Evaluation of Parameters on Carbon Produced

The purpose of Task 4 is to develop a system in which the products of the reaction can be isolated for easy analysis and the effects of changing parameters can be evaluated.

In molten salt reactions, the only analytical technique that could differentiate carbon produced in one reaction from another is the SEM. XRD patterns only differed in byproduct identification. Raman spectra showed graphitic and amorphous carbon in all samples. Since only one carbide and one salt appeared to be suitable for solvent-phase reactions, reduction potential is no longer a variable for solvent-phase reactions. This significantly reduced the number of potential parameters on later solvent-phase reactions.

Solvent-phase reactions (discussed in Task 5) were conducted in the proposed reactor, shown in Figure 1. Reaction parameters include:

1. Solvent
2. Carbide particle size
3. Reactor configuration (discussed in Task 5)

Initially, salt concentration was considered as a parameter. However, it is difficult (impossible with available equipment) to maintain an arbitrary concentration below the solubility limit. As a solvent-phase reaction proceeds, the salt is consumed and thus concentration decreases. To maintain an arbitrary concentration, fresh salt would have to be added at exactly the rate it is consumed by the reaction. Alternatively, enough solvent and salt could be used that the concentration would not appreciably change as the carbide is consumed. However, if excess salt is present (more than can be dissolved

in the solvent) then the excess salt would be dissolved as dissolved salts are consumed via the reaction. In short, having excess salt will automatically maintain the salt concentration at the solubility limit of the salt.

Solvents used were methanol and ethanol, based on Task 3 experiments. The expected result was that methanol would have a higher desired reaction rate because both salts are more soluble. However, it was also shown that the undesired reaction happens more quickly with methanol. So it was hypothesized that there would be a tradeoff of more favorable kinetics with less favorable selectivity.

Calcium carbide is available in large pieces (1-5 cm). Solvent-phase reactions were conducted with large, single pieces and with a fine powder (100 mesh). This was expected to have a similar tradeoff to solvent choice: kinetics versus selectivity. Based on experiments in Task 3, it is expected that smaller pieces will favor the undesired reaction.

Two primary reactor configurations were developed, as discussed in Task 5. The primary difference between these two reactor configurations is the salt bridge. One reactor was equipped with a glass frit. The other reactor was equipped with an anion exchange membrane. The expected result is that the frit will allow for more ion transfer, but will also allow for some bulk material transfer. The anion exchange membrane will be selective and only allow chloride anions to pass through, but the rate of ion flow will be lower than the glass frit.

4.5. Task 5 – Design of a system to Control Reaction

The purpose of a two-cell reactor is to force the reaction to take place in two separate locations: the oxidation reaction takes place on the anode, and the reduction reaction takes place on the cathode. To understand reactor design, it is important to understand some basic electrochemistry. The overall reaction is:

The two half reactions are:

Note that calcium and chlorine do not change oxidation state, so they are spectator ions and thus have no half reactions.

The reaction apparatus is shown in Figure 1 (shown again for convenience).

Figure 1 – 2-cell Experimental Setup

The oxidation of carbide anion takes place on the calcium carbide, shown on the right. Two chloride anions from solution remove a calcium cation from calcium carbide and make calcium chloride. This leaves elemental carbon behind and liberates two electrons. These electrons flow through the pieces of carbide (This is critical! Since calcium carbide is acting as an electrode, it must be electrically conductive. Fortunately, it is somewhat conductive.) through the wire to the zinc cathode. These electrons move to the zinc metal rod and reduce zinc cations from solution to produce zinc metal. This frees two chloride anions, which flow to the other cell through the salt bridge. These reactions can be thought of as follows (note, these are not proper half reactions):

The practical benefits of using a two-cell reactor over reactions done in Task 2 are several:

1. Simplified cleaning
2. Measured reaction rate
3. Controlled reaction potential

The cleaning procedure will be simplified because there will be no metal near the carbide. If the reaction goes to completion, filtering will be sufficient to clean, since the cell will only contain dissolved calcium chloride and carbon. An ammeter placed in the wire will show the current flow. This current flow can be converted to reaction rate via Faraday's Law. A potentiostat can control the potential between the two cells.

The potentiostat is placed in series where the wire is. Potentiostats also require a reference electrode. A Ag|AgCl (read as “silver-silver chloride”) reference electrode was used. Preparation of this electrode is described in the Appendix. The reference electrode was placed in the carbide cell. Potentiostats have two modes: active, set a voltage is maintained (the available potentiostat has a range of +/- 14 V), or passive, the potentiostat is essentially a multi-meter. When passive, the reaction is said to be galvanic.

The focus of reactor design was on the salt bridge. The purpose of the salt bridge in this reactor is to allow chloride anions to flow to the carbide cell while preventing zinc cations from flowing to the carbide. If zinc cations make it to the carbide cell, then both reactions occur on the surface of the carbide. This effectively shorts out the cell. The reaction will happen without causing electron flow through the wire.

Some typical designs for salt bridges are filter paper, glass U-tubes, and glass frits. Since these reactions are highly sensitive to water, the reactor must be sealed. This effectively removed filter paper bridges from consideration. Glass U-tubes allow mass transfer, and require an additional, intermediate salt. This left glass frits as the most preferred option. A glass reactor was constructed following the design shown in Figure 1 using a glass frit. This reactor was used for several experiments. The first experiment simply verified that the reaction could take place in a 2-cell arrangement.

4.5.1. Glass-Frit Reactor Experiment 1 – Proof of Concept

An experiment was conducted to determine if the proposed reactions occur in a 2-cell reactor, as shown in Figure 1.

Materials

- 500 g ZnCl_2
- 9" x $\frac{1}{4}$ " zinc rod
- 6.6 g CaC_2
- 750 mL methanol
- 200 g CaCl_2
- 500 mL concentrated HCl
- Distilled water

Equipment

- Potentiostat
- 2-Cell reactor with glass frit
- Ag|AgCl reference electrode
- 2 x magnetic stir plates
- Borosilicate glass-fritted filter and vacuum assembly

Procedure

Zinc chloride was added to 250 mL of methanol. This was stirred in a sealed flask for 1 hour. This produced a saturated zinc chloride-methanol solution. The solution, along with remaining, undissolved zinc chloride, was added to the left cell. Calcium chloride was added to 500 mL of methanol. This was stirred in a sealed flask for 1 hour. (Since calcium cations and chloride anions are spectators, they do not affect the thermodynamics of the reaction. Calcium chloride is added to provide initial chloride anions.) This solution was added to the right cell.

A single piece of calcium carbide was placed in a platinum crucible. This crucible was suspended by a platinum wire. Note that once the metal is above the height of liquid, platinum does not have to be used. The wire can only act as a path for electrons, since it is not in an electrolytic solution.

The platinum wire was attached to a copper wire, which was connected to positive port on the potentiostat. Another wire connected the negative port to the zinc rod. The zinc rod was submerged into the zinc-chloride methanol solution. (Not shown on the diagram are ground glass fittings that go on top of each cell. This effectively seals the entire assembly.)

The potentiostat was set to passive mode (galvanic), and the valve on the salt bridge was opened. Current was monitored using data acquisition software. The reaction was allowed to proceed for 72 hours. The platinum crucible was removed, and the contents were added to dilute hydrochloric acid. The remaining material was then filtered, and analyzed via SEM and EDS.

Results

The current was initially measured to be 145 μA . Over the course of the reaction, the current did not appreciably change.

Figure 25 – Current change of the course of 4.5.1. Glass-Frit Reactor Experiment 1 – Proof of Concept

The four drops in current were the result of an electrode clip coming loose.

Gas was evolved during the reaction. Some of the original piece of calcium carbide was visible after reaction. White powder was found in the cell. After cleaning with acid and filtration, a coarse black powder remained. Single pieces appeared larger than previous molten-salt reactions. The mass of carbon produced was approximately 30 mg. Note that when the mass is this small, material that adheres to the filter is most likely a significant amount. This mass corresponds to 1.3% completion, with respect to the desired reaction.

Figure 26 – Zoomed out SEM image. Note the large pieces.

Figure 27 – Image of Products. All products showed essentially pure carbon. Note the angular edges and sheets, indicative of graphite.

Figure 28 – More flat, layered crystals. Note the crystal on the right appears to have a hexagonal structure, indicative of high-quality graphite.

EDS (not shown) showed the sample to be essentially pure carbon. Silica impurities were found. This impurity comes from calcium carbide production, and cannot be removed. (HF can remove it, but was not used out of safety concerns.) Trace amounts of zinc were detected.

Conclusions

It appears that the reaction occurred as expected in a two-cell system. Morphology appears to be significantly different than molten-salt reactions. Larger single crystal size typically results from slower formation. Since the molten-salt reactions occur at much higher temperatures, the reaction rate will be higher. Additionally, molten salt reactions were conducted with crushed calcium carbide to ensure homogeneity. This reaction was conducted with a large, single piece. This reduces surface area, which reduces reaction rate.

The accumulated current that was measured accounts for 33.8 coulombs. This equates to 10^{-4} moles of carbon, or 9.6 mg of carbon. The current measured does not account for all (or even most) of the carbon formed. This means that the reaction was shorted. Some zinc chloride must have crossed the salt bridge and reacted on the surface. This means that the salt bridge was ineffective. While other reactions were conducted with this cell, discussion will focus on the second 2-cell reactor design. This reactor replaced the glass frit with an anion exchange membrane.

4.5.2. Anion-Exchange-Membrane Reactor Experiment 1 – Proof of Concept

An experiment was conducted to determine if the proposed reactions occur in a 2-cell reactor, as shown in Figure 1. The glass frit was replaced with an anion exchange membrane. This membrane physically resembles a thick piece of flesh colored plastic.

Materials

- 500 g ZnCl_2
- 9" x $\frac{1}{4}$ " zinc rod
- 7.6 g CaC_2
- 750 mL methanol
- 200 g CaCl_2
- 500 mL concentrated HCl
- Distilled water

Equipment

- Potentiostat
- 2-Cell reactor with anion exchange membrane
- Ag|AgCl reference electrode
- 2 x magnetic stir plates
- Borosilicate glass-fritted filter and vacuum assembly

Procedure

Zinc chloride was added to 250 mL of methanol. This was stirred in a sealed flask for 1 hour. This produced a saturated zinc chloride-methanol solution. The solution, along

with remaining, undissolved zinc chloride, was added to the left cell. Calcium chloride was added to 500 mL of methanol. This was stirred in a sealed flask for 1 hour. (Since calcium cations and chloride anions are spectators, they do not affect the thermodynamics of the reaction. Calcium chloride is added to provide initial chloride anions.) This solution was added to the right cell.

A single piece of calcium carbide was placed in a platinum crucible. This crucible was suspended by a platinum wire. Note that once the metal is above the height of liquid, platinum does not have to be used. The wire can only act as a path for electrons, since it is not in an electrolytic solution.

The platinum wire was attached to a copper wire, which was connected to positive port on the potentiostat. Another wire connected the negative port to the zinc rod. The zinc rod was submerged into the zinc-chloride methanol solution. (Not shown on the diagram are ground glass fittings that go on top of each cell. This effectively seals the entire assembly.)

The potentiostat was set to passive mode (galvanic), and the valve on the salt bridge was opened. Current was monitored using data acquisition software. The reaction was allowed to proceed for 72 hours. The platinum crucible was removed, and the contents were added to dilute hydrochloric acid. The remaining material was then filtered, and analyzed via SEM and EDS.

Results

The current was notably lower for this reaction. The current reached was approximately 90 μA throughout the 72 hours. It did not change appreciably.

Gas was evolved during the reaction. Some of the original piece of calcium carbide was visible after reaction. White powder was found in the cell. After cleaning with acid and filtration, a coarse black powder remained. Single pieces appeared larger than previous molten-salt reactions. The mass of carbon produced was approximately 25 mg.

Figure 29 – Low magnification image of 4.5.2. Anion-Exchange-Membrane Reactor Experiment 1 – Proof of Concept. Larger pieces seem more abundant.

Fewer small pieces appeared to be present. Large, layered pieces of pure carbon were abundant. Note the flaky structure in the center of Figure 29.

Figure 30 – Single, hexagonal crystals in the sample. Note the non-conductive material on the left. EDS showed this to be silica.

Significant silica appeared in this sample. Silica is a contaminant in some calcium carbide. Although it appears significant in Figure 30, silica accounted for less than 1 wt% of the sample, when large sections were analyzed. No zinc was found in the sample.

Conclusions

The ion exchange membrane appears to have worked. No zinc migrated, and the reaction occurred as predicted. The mass of the sample should have been 5.8 mg, as predicted by the accumulated current. It is unclear where the excess carbon came from. Some of the mass was contaminants in the calcium carbide (silica, for example). Some of it was leftover coke from calcium carbide synthesis. However, neither of these account for the quantity observed. It was never conclusively discovered where the excess carbon comes from.

Large amounts of white powder were observed. This indicates the formation of calcium methoxide from the undesirable reaction between calcium carbide and methanol. 7.6 g of calcium carbide should produce 2.85 g of carbon, if the reaction were to go to completion. The mass of 25 mg corresponds to a completion of 0.8% with respect to the desired reaction. This means that far too much of the calcium carbide is consumed by methanol. Future experiments focused mainly on using ethanol, as it does not apparently consume the carbide (at least on interesting timescales).

Since the ion exchange membrane has been shown to work, additional experiments utilized the ion exchange membrane. Remaining variables to be tested include the application of a potential via the potentiostat, use of ethanol in two-cell configurations, and the impact of particle size on the reaction rate, selectivity, and morphology of carbon produced.

One additional experiment was performed using methanol, but with crushed calcium carbide. The purpose of this experiment was to see if increased surface area increased the desired reaction (the carbon-producing reaction) more quickly than it increased the undesired reaction (the methoxide-producing reaction).

4.5.3. Anion-Exchange-Membrane Reactor Experiment 2 – Small Particle Size

An experiment was conducted to determine if the proposed reactions occur in a 2-cell reactor, as shown in Figure 1. The reactor utilized an anion-exchange membrane and crushed calcium carbide.

Materials

- 500 g ZnCl_2
- 9" x $\frac{1}{4}$ " zinc rod
- 5.0 g CaC_2
- 750 mL methanol
- 200 g CaCl_2
- 500 mL concentrated HCl
- Distilled water

Equipment

- Potentiostat
- 2-Cell reactor with anion exchange membrane
- Ag|AgCl reference electrode
- 2 x magnetic stir plates
- Borosilicate glass-fritted filter and vacuum assembly

Procedure

Zinc chloride was added to 250 mL of methanol. This was stirred in a sealed flask for 1 hour. This produced a saturated zinc chloride-methanol solution. The solution, along with remaining, undissolved zinc chloride, was added to the left cell. Calcium chloride was added to 500 mL of methanol. This was stirred in a sealed flask for 1 hour. (Since calcium cations and chloride anions are spectators, they do not affect the thermodynamics of the reaction. Calcium chloride is added to provide initial chloride anions.) This solution was added to the right cell.

The platinum wire was attached to a copper wire, which was connected to positive port on the potentiostat. Another wire connected the negative port to the zinc rod. The zinc rod was submerged into the zinc-chloride methanol solution. (Not shown on the diagram are ground glass fittings that go on top of each cell. This effectively seals the entire assembly.)

Calcium carbide was crushed in the glove box to 100 mesh and added to a platinum crucible. The crucible was sealed in a bottle. Once the cells were prepared, the crucible was removed from the bottle and suspended in the platinum cage. This was done to minimize the exposure of the finely ground calcium carbide to air.

The potentiostat was set to passive mode (galvanic), and the valve on the salt bridge was opened. Current was monitored using data acquisition software. The reaction was allowed to proceed for 72 hours. The platinum crucible was removed, and the contents were added to dilute hydrochloric acid. The remaining material was then filtered, and analyzed via SEM and EDS.

Results

Essentially no current was measured. It could have been below the threshold of detection for the potentiostat (1 μA). As the crucible was lowered into the calcium cell, the fine carbide powder was stirred up, and gas was immediately produced. After cleaning with acid, no visible solids remained.

Conclusions

It appears that the undesired reaction rate increased much more than the desired.

Additionally, the practical difficulty of lowering a finely ground, reactive powder into a liquid should not be discounted. Carbide spilled out of the platinum crucible. Since the carbide that spilled was no longer in electrical contact with the rest of the cell, it could not participate in the desired reaction. (The electrons had nowhere to go.)

A possible solution is to use an intermediate particle size. Because of the nature of calcium carbide, intermediate particle sizes are difficult to produce. When crushing calcium carbide, large pieces tend to turn directly to dust.

Based on these experiments, methanol has been removed as a solvent for two-cell reactions. It is too reactive with calcium carbide to be of use. Future experiments focused on ethanol using a reactor with an anion-exchange membrane. Zinc chloride is less soluble in ethanol than in methanol, so it is unclear how this will affect the reaction rate.

4.5.4. Anion-Exchange-Membrane Reactor Experiment 3 – Ethanol, large particle
An experiment was conducted to determine if the proposed reactions occur in a 2-cell reactor, as shown in Figure 1, with ethanol as a solvent.

Materials

- 500 g ZnCl_2
- 9" x $\frac{1}{4}$ " zinc rod
- 5.0 g CaC_2
- 750 mL ethanol
- 200 g CaCl_2
- 500 mL concentrated HCl
- Distilled water

Equipment

- Potentiostat
- 2-Cell reactor with anion exchange membrane
- Ag|AgCl reference electrode
- 2 x magnetic stir plates
- Borosilicate glass-fritted filter and vacuum assembly

Procedure

Zinc chloride was added to 250 mL of ethanol. This was stirred in a sealed flask for 1 hour. This produced a saturated zinc chloride-ethanol solution. The solution, along with

remaining, undissolved zinc chloride, was added to the left cell. Calcium chloride was added to 500 mL of ethanol. This was stirred in a sealed flask for 1 hour. (Since calcium cations and chloride anions are spectators, they do not affect the thermodynamics of the reaction. Calcium chloride is added to provide initial chloride anions.) This solution was added to the right cell.

The platinum wire was attached to a copper wire, which was connected to positive port on the potentiostat. Another wire connected the negative port to the zinc rod. The zinc rod was submerged into the zinc-chloride ethanol solution. (Not shown on the diagram are frosted glass fittings that go on top of each cell. This effectively seals the entire assembly.)

A single piece of calcium carbide was placed in a platinum crucible. This crucible was suspended by a platinum wire. Note that once the metal is above the height of liquid, platinum does not have to be used. The wire can only act as a path for electrons, since it is not in an electrolytic solution.

The potentiostat was set to passive mode (galvanic), and the valve on the salt bridge was opened. Current was monitored using data acquisition software. The reaction was allowed to proceed for 72 hours. The platinum crucible was removed, and the contents were added to dilute hydrochloric acid. The remaining material was then filtered, and analyzed via SEM and EDS.

Results

Current of 46 μA was additionally observed, and it rose, discontinuously, up to 130 μA .

Figure 31 – Current change for 4.5.4. Anion-Exchange-Membrane Reactor Experiment 3 – Ethanol, large particle. Note the steps.

No white powder was present, and much of the calcium carbide was left intact, releasing acetylene upon cleaning. After cleaning, 7 mg of material remained. It was a coarse, black powder similar to that found in previous 2-cell reaction. EDS showed similar quantities of silica to previous experiments (< 1wt%).

Figure 32 – Two large, hexagonal, carbon crystals.

Figure 32 shows two hexagonal carbon crystals. The right edge of the two appears to line up, while the top crystal did not grow as large as the bottom. The top left corner appears to have been mechanically damaged. Individual sheets of graphite appear to have pulled away. Contaminants on the periphery are silica.

Figure 33 – Another large, hexagonal crystal from 4.5.4. Anion-Exchange-Membrane Reactor Experiment 3 – Ethanol, large particle.

Error! Reference source not found. shows another hexagonal crystal. This one appears more regular than previous. Again, mechanical deformation appears to have shifted the top few layers. Notice how the sheets are transparent at the top. This means that the sheets are very thin.

Figure 34 – Edge of hexagonal crystal. Notice the layers of carbon that form a graphite crystal.

Conclusions

Ethanol appears to be a suitable solvent for the 2-cell reactor. Carbon similar to what was formed with methanol was produced. Ethanol had the effect of decreasing the desired reaction rate, but it virtually eliminated the side reaction (very little white precipitate was formed).

The desired reaction rate, as measured by current flow, increased monotonically over the course of the experiment. This could be caused by increased conductivity of the surface. As graphite forms on the surface of the carbide, a larger percentage of the reactive surface area is conductive. (Graphite is much more conductive than calcium carbide.)

4.5.5. Anion-Exchange-Membrane Reactor Experiment 4 – Ethanol, small particle
An experiment was conducted to determine if the proposed reactions occur in a 2-cell reactor, as shown in Figure 1, with ethanol as a solvent and crushed calcium carbide.

Materials

- 500 g ZnCl_2
- 9" x $\frac{1}{4}$ " zinc rod
- 5.0 g CaC_2
- 750 mL ethanol
- 200 g CaCl_2
- 500 mL concentrated HCl
- Distilled water

Equipment

- Potentiostat
- 2-Cell reactor with anion exchange membrane
- Ag|AgCl reference electrode
- 2 x magnetic stir plates
- Borosilicate glass-fritted filter and vacuum assembly

Procedure

Zinc chloride was added to 250 mL of ethanol. This was stirred in a sealed flask for 1 hour. This produced a saturated zinc chloride-ethanol solution. The solution, along with remaining, undissolved zinc chloride, was added to the left cell. Calcium chloride was added to 500 mL of ethanol. This was stirred in a sealed flask for 1 hour. (Since calcium cations and chloride anions are spectators, they do not affect the thermodynamics of the reaction. Calcium chloride is added to provide initial chloride anions.) This solution was added to the right cell.

The platinum wire was attached to a copper wire, which was connected to positive port on the potentiostat. Another wire connected the negative port to the zinc rod. The zinc rod was submerged into the zinc-chloride methanol solution. (Not shown on the diagram are ground glass fittings that go on top of each cell. This effectively seals the entire assembly.)

Calcium carbide was crushed in the glove box to 100 mesh and added to a platinum crucible. The crucible was sealed in a bottle. Once the cells were prepared, the crucible was removed from the bottle and suspended in the platinum cage. This was done to minimize the exposure of the finely ground calcium carbide to air.

The potentiostat was set to passive mode (galvanic), and the valve on the salt bridge was opened. Current was monitored using data acquisition software. The reaction was allowed to proceed for 72 hours. The platinum crucible was removed, and the contents were added to dilute hydrochloric acid. The remaining material was then filtered, and analyzed via SEM and EDS.

Results

Essentially no current was measured. It could have been below the threshold of detection for the potentiostat (1 μ A). As the crucible was lowered into the calcium cell, the fine carbide powder was stirred up, however, no gas was noticed. After cleaning with acid, no visible solids remained.

Conclusions

It appears that the undesired reaction rate increased much more than the desired.

Additionally, the practical difficulty of lowering a finely ground, reactive powder into a liquid should not be discounted. Carbide spilled out of the platinum crucible. Since the carbide that spilled was no longer in electrical contact with the rest of the cell, it could not participate in the desired reaction. (The electrons had nowhere to go.)

A possible solution is to use an intermediate particle size. Because of the nature of calcium carbide, intermediate particle sizes are difficult to produce. When crushing

calcium carbide, large pieces tend to turn directly to dust. Based on these experiments, small particle size is not recommended for use in these reactions.

4.5.6. Summary of Task 5 Conclusions

Based on experiments performed in Task 5, both methanol and ethanol appear to function as solvents for the oxidation of the carbide anion. Notably, this is the first time the carbide anion has been oxidized at ambient conditions, and the first time it has been reduced in solution. Additionally, the morphologies produced (layered hexagons) have not been seen in literature. Raman spectroscopy and electron microscopy indicate highly ordered crystal structure. This makes sense, as the formation of the crystals happens at such low energy that defects cannot easily form. Normally, low energy means low rate of formation. However, since these reactions were carried out in solution, concentrations are very high. Thus rates can still be (relatively) high. Methanol appears to have a higher rate, as determined by the current. However, methanol also has a much faster side reaction.

Both the glass frit and anion-exchange membrane worked successfully. However, the glass frit appears to allow chloride anions to migrate to the carbide cell. This shorts the reaction out, and allows the reaction to proceed at a voltage not controlled by the potentiostat.

Reducing the particle size of the carbide appears to increase the side reaction much more quickly than the desired reaction, even with ethanol. The optimal condition appears to be large, single crystals.

5. Summary of Key Results and Conclusions

Each task performed in this research uncovered new information.

Task 1 established which analytical techniques would be useful. SEM-EDS provided the bulk of analysis. Raman spectroscopy provided strong evidence for which forms of carbon were produced, but can only analyze one crystal at a time. XRD provided weaker evidence of what types of crystals were produced for an entire sample. Additionally, techniques for purifying the carbon products were developed. No exotic reagents are required for purification.

Task 2 established that carbides do react with low-melting point salts at mild conditions to produce various morphologies. CaC_2 reacts with ZnCl_2 and SnCl_2 while Al_4C_3 reacts with SnCl_2 . This was the first time that these reactions have been performed and the first time that carbon was produced via redox at such mild conditions. Additionally, carbon of varying forms was produced.

Task 3 showed that some of the redox reactions explored in Task 2 could occur in a solvent. Specifically, CaC_2 reacts with ZnCl_2 in both methanol and ethanol. However, methanol has a significant side reaction. This was the first time that these reactions were carried out in a solvent. The conditions were the mildest conditions known to reduce the carbide anion.

Task 4 studied what effects would be important for later solvent-phase reactor designs. It was decided that choice of solvent, particle size, and reactor configuration. Reactor configuration varied by changing the mass-transfer limiting barrier. The two choices

were a glass frit and an anion-exchange membrane. Commercially-available anion exchange membranes were shown to be compatible with both solvents chosen in Task 3.

Task 5 showed that the solvent-phase redox reactions explored in Task 3 could occur as separated, half-cell reactions. The advantages of this are two-fold: a simplified purification procedure and direct measurement of the reaction rate. Since the metals are reduced in a separate cell, they would not have to be removed from the desired carbon material. Since the reaction is forced to take place through two half reactions, the rate could be measured via current.

Both ethanol and methanol showed measurable carbon production. However, methanol reacted much more quickly with calcium carbide to produce an undesired product. Ethanol reacted more slowly, and produces nearly negligible amounts of undesired product.

Carbon produced via half-cell, solvent-phased reaction showed a unique, layered, hexagonal structure. (While graphite is hexagonal, it does not typically produce micron-scale hexagonal crystals.) This has not been seen in literature before. Raman and SEM analysis indicate that this carbon is highly ordered.

6. Recommendations

Future areas of research should include:

(1) **Isolation of carbon allotropes.** While XRD provided evidence that graphite and diamond was produced, these two forms could not be isolated. Being able to separate these phases would allow for quantification of yields of each phase. Potential routes to this include density separation and selective oxidation.

(2) Yield quantification would in turn allow for **optimization of reaction conditions.**

Different conditions may allow for higher yield of one phase over the other. This would be especially useful in scaling the process up to an industrial process. Additionally, crystal size may be controlled by altering reaction conditions.

(3) Separation and optimization may allow for isolation of the large, hexagonal crystals.

This would allow for **analysis of the electronic and physical properties of the hexagonal crystals.** Crystals like this have not been observed. These crystals may be easily separated into small sheets. If so, this could be a potential route to producing graphene.

(4) **Synthesis of purer or different carbides** will remove any effects caused by iron impurities seen in commercial calcium carbide. Additionally, unavailable carbides may show still more morphologies.

7. Appendix

7.1. Preliminary Experiments

Preliminary experiments on several of the proposed reactions have been completed.

From these experiments, several important facts have been determined. The most important findings of the initial experiments were: the reactions occur as hypothesized, molten salts react quickly with stainless steel, and reactors must be charged in an oxygen and moisture free environments. During these reactions, no cleaning procedure was used. The raw product from the reactions were taken to be analyzed.

Preliminary Experiment 1

The first reaction that was done was with aluminum carbide and stannous fluoride:

The reactants were loaded into a stainless steel reactor which was sealed with a copper gasket. At this time it was thought that moisture from the atmosphere would have a negligible effect on the reaction, so it was loaded at ambient conditions. Stoichiometric amounts of reactants were charged. The reactor was placed into a heated sand bath which was set to 235°C (m.p. of stannous fluoride is 215°C) and the reaction was allowed to run for 1 hour. To prevent a pressure buildup from any moisture that was absorbed during loading, the reactor was connected to a vacuum line through a water bubbler via stainless steel tubing.

Figure 35- Initial reactor setup

When the reaction reached temperature, the tubing connecting the reactor to the bubbler melted. This is because the reaction is very exothermic. Prior to running the reaction, it was thought that the heat mass of the reactor would be sufficient to maintain a nearly constant temperature even though the reaction is exothermic. However, aluminum carbide is a very fine powder, so the reaction likely happened very quickly. Moreover, the heat of reaction is approximately -8800 kJ/mol. (This is more than three times the heat of combustion of propane on a mole basis.) The primary reason for this is aluminum fluoride's very negative heat of formation. The vacuum prevented any reactants or products from reaching the environment, and nobody was harmed.

The contents of the reaction were taken to the SEM for analysis. The purpose of the analysis was to see if the reaction happens as predicted. If so, the products should all be present.

Figure 36- Micrograph and EDS of products of Preliminary Reaction 1

This shows that aluminum fluoride is present, and suggests that the reaction proceeded as hypothesized.

Initially, it was thought that stainless steel would not react significantly with the reactants at the temperatures and in the timescales of interest. Thus the reactants could be loaded directly into a stainless steel reactor. This was proven to be incorrect. The salts are so corrosive when molten that chromium is extracted from the stainless steel to form chromium (III) chloride. Chromium chloride hexahydrate, $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$, is a transparent dark green crystal that is soluble in water. Because of this, subsequent preliminary reactions were done in glassware.

Preliminary Reaction 2

The second reaction to be performed used stannous fluoride again, but with calcium carbide instead.

Calcium fluoride has a much more positive heat of formation than aluminum fluoride, so this reaction is not nearly as exothermic (-3500 kJ/mol). Additionally, calcium carbide is much coarser than aluminum carbide, so mass transfer will slow the reaction, allowing more time for heat to dissipate. The reactor was loaded stoichiometrically and placed into the heated sand bath at 235°C for 1 hour. The contents were removed, and analyzed with the SEM and EDS. The results can be seen in the following figures.

Figure 37 - Tin beads formed from Preliminary Reaction 2

Figure 37 shows spheres of tin. Again, this suggests that the reaction occurs as intended. Other peaks on the EDS are likely to be noise or contaminants. The tin forms in spheres as it cools and solidifies, as the reaction is run above the melting point of tin (230°C).

Figure 38 – Carbon Plates from Preliminary Reaction 1

Figure 38 shows the remaining product, carbon. The EDS confirms the presence of carbon. (It should be noted that carbon is unusual when analyzed with EDS. A very small peak can indicate a large amount of carbon.) The morphology of the carbon appears to be stacks of flat sheets, indicative of sp^2 hybridization. This could potentially be sheets of loosely bound graphite. The micrograph and elemental analysis is not conclusive of this, however.

Figure 39 – Micrograph and EDS of Preliminary Reaction 2

In Figure 39, spheres of tin can be seen. Additionally, cubic crystal structures are present, which indicates the presence of calcium fluoride. This suggests that this reaction occurred as hypothesized also.

Figure 40 – Carbon Sheets produced in Preliminary Reaction 2

Figure 40 shows thin carbon sheets, which are nearly pure carbon. The surface sheets are thin enough to be transparent to the electron beam at 10kV. This implies that the carbon is very thin (10s of atoms at most). XRD analysis (not shown) did not show the presence of any known types of graphite. This could imply that the sheets are too thin to have a typical graphite peak, and thus are graphene. This is not conclusive, and Raman spectroscopy was not available at the time.

Preliminary Reaction 3

The third reaction was of calcium carbide and stannous chloride (m.p. 247°C).

Stoichiometric amounts were loaded into the glass reactor. The contents were heated to 285°C and allowed to react for 1 hour. The reactor was then removed from the sand bath, and allowed to cool. The contents were removed from the reactor and analyzed.

Figure 41 – Calcium chloride crystals

Figure 41 shows a crystal of calcium chloride. The crystal is large non-conductive, so it “charges”. The electrons from the electron beam have no path to ground, so they collect above the sample creating the shimmering seen in the figure. This is common with ionic compounds. These results also support the original hypothesis that the carbides can react at lower temperatures by reducing metallic cations with lower oxidation potentials.

7.2. Nernst Equation

When considering redox reactions, cell potentials and thus spontaneity can be determined by the Nernst equation, Equation 25. The Nernst equation comes directly from the definition of Gibbs energy.

$$E_{red} = E_{red}^{\circ} + \frac{RT}{nF} \ln \frac{\alpha_{ox}}{\alpha_{red}} \quad (19)$$

The Nernst equation relates the half-cell reduction potential, E_{red} , in an electrochemical cell to temperature, reaction quotient, and standard reduction potentials. The potential is with respect to a standard hydrogen electrode, which has a defined potential of 0 V. It should be noted that the same is true for an oxidation reaction, except for a sign change. The total cell potential is the sum of the two half-cell potentials. Convention is to consider all reactions as reduction reactions. (Oxidation reactions are reduction reactions in reverse.)

In Equation 25, R is the universal gas constant, T is absolute temperature, n is the number of electrons transferred per stoichiometric reaction, F is Faraday's constant, and α is the activity of each species. For pure solids and liquids, the activity is defined as unity. For dilute dissolved substances, the activity can be approximated as the molar concentration of the solute, C_i , raised to its stoichiometric coefficient, ν_i . In this case, the ratio of activities reduces to the more common reaction quotient, $\prod C_i^{\nu_i}$. (In dilute systems, the activity is approximated as the ratio of the molar concentration of a substance to standard molar concentration. The standard molar concentration is 1 M, so as long as standard units are used, this has no quantitative effect.)

For pure substances, such as are present in the molten reactions, the activities are all unity, and thus the reduction half-cell potential reduces to the standard reduction potential. However, in the molten reactions, the cells are not divided, so it is impossible to measure the half-cell potentials.

For dissolved substances, such as would be present in the solvent-phase reactions, the concentration becomes relevant. As the reactants are depleted, the half-cell potential decreases. By Ohm's law, assuming constant resistance, a decreased potential has the effect of decreasing the current. Current is proportional to reaction rate (Faraday's constant being the proportionality). So, as is typical, as reactants are depleted, the reaction rate decreases.

The hypothesis is, however, that different potentials may create different allotropes of carbon. This means that as the reaction begins, one allotrope could be formed. Then, as the potential decreases, a different (possibly undesired) allotrope is formed. So it may be desired to maintain a constant potential. This can be accomplished in two ways: by maintaining concentration (and thus activity) throughout the reaction, or by applying a potential. Both routes should be investigated.

Maintaining concentration could be done by having excess (in terms of solubility, not stoichiometry) salt present. This would ensure a saturated solvent. A constant potential could be achieved by using a potentiostat. Potentiostats are standard pieces of hardware, and readily available.

7.3. Calcium Carbide Control Experiment

An experiment was performed to determine the inherent carbon content of calcium carbide. This was done to provide further evidence that carbon collected during this research was indeed produced via the proposed reactions and not an impurity.

Materials

- 257.4 g calcium carbide, several pieces
- 200 mL concentrated hydrochloric acid
- 500 mL distilled water

Equipment

- 1000 mL borosilicate beaker
- Magnetic stir plate
- Borosilicate glass-fritted filter and vacuum assembly

Procedure

Some calcium carbide was placed in the tall-form beaker. The beaker was placed in a fume hood. 250 mL of distilled water was added. The solution was stirred on the stir plate until visible evidence of a reaction stopped. The 14 M hydrochloric acid was added to the rest of the distilled water and stirred. This diluted hydrochloric acid was then added to the beaker containing the calcium carbide. This was allowed to stir overnight. Any magnetic material was allowed to remain on the stir bar. The clean filter was weighed. The remaining material was filtered the next day using the glass-fritted filter assembly. This process was repeated until all the calcium carbide had been consumed. The filter was then dried in an oven at 80°C and weighed again.

Safety

Acetylene gas will be released when water and/or acid is added to calcium carbide.

Because of this, the experiment was performed in a fume hood. Additionally, gloves resistant to acid, goggles, and a lab apron must be worn.

Results

Very little material remained on the filter after the first batch of carbide was filtered.

This is the reason that so much calcium carbide had to be used. The difference in weight on the filter was measured to be 0.55g. This implies that the calcium carbide used has approximately 0.2 wt% non-magnetic material. This material was analyzed via EDS and determined to be amorphous carbon.

Conclusions

Calcium carbide is produced using coke. From this experiment, it can be said that it has very little unreacted coke leftover. Any elemental carbon that is produced in excess of 0.2 wt% of the calcium carbide can be attributed to a reaction.

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