Executive Summary

This thesis examines the reaction in which deuterium hydride gas (HD) forms from hydrogen gas (H₂) reacting with deuterium gas (D₂), and the reverse reaction in which HD reacts with itself to from H₂ and D₂ and how it is catalyzed by metal-organic frameworks. Metal-organic frameworks (MOFs) are composed of metal oxide clusters joined into an ordered structure by organic ligands. We found previously that in the presence of a specific type of MOF, MOF-74, a mixture of H₂ and D₂ gas to react and form HD gas at room temperature. We did not expect this reaction to occur due to the high energy barrier, on the order of 500 kJ/mol (equivalent to a temperature of 60,000 K). MOFs are advantageous for catalysis for many reasons including that due to their porous nature, they have no “dead volume” in which catalysis cannot occur. MOFs have been used to intentionally catalyze many reactions, but we were unable to find another instance of MOFs catalyzing the formation of HD in the literature. HD gas has however been formed experimentally in other ways, but the only methods that do not use high temperatures involve transition metal catalysis or catalysis at paramagnetic centers.

We investigated how the reaction rate depended on temperature and pressure. We monitored the reaction using a triple-filter quadropole mass spectrometer, which can distinguish H₂, D₂, and HD by their molecular masses. Two different MOF-74 samples were studied, a 60 mg sample of Ni₂(dopbdc) and a 900 mg sample of Co₂(dobdc). We found that with both samples, the MOF-catalyzed reaction occurred noticeably at temperatures from 23°C to 125°C. The reaction rate increased with temperature as expected, and both samples had activation energies on the order of 7 kJ/mol, much less than the 500 kJ/mol for the uncatalyzed reaction. Thus the presence of the MOF powder creates a low-energy pathway for the reaction to happen. The reaction rate increased with pressure, with a linear or slower-than-linear relationship. In conclusion, we have confirmed that the HD formation is a real effect with a very low activation energy, and that it appears to be mostly a first-order process.
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Chapter 1

Motivation and Background

1.1 Motivation

1.1.1 Hints of HD formation

While performing experiments to separate hydrogen gas and deuterium gas using a metal-organic framework called MOF-74, the formation of deuterium hydride gas (HD) was observed on the timescale of minutes to hours at room temperature using both mass spectrometry and infrared spectroscopy. At first glance, this reaction seems implausible at room temperature - forming HD must involve breaking a H-H bond (and a D-D bond) which has a bond energy of 432 kJ/mol [1]. According to Arrhenius’s Law, the exponential factor of the rate constant of this reaction at room temperature is $e^{-E_a/RT} \approx 10^{-76}$, indicating that the uncatalyzed reaction is incredibly unlikely, and thus incredibly slow. The presence of the MOF must provide a lower-energy alternate pathway for the reaction to occur. However, there is no known mechanism in the literature. This thesis investigates the kinetics of this reaction in an attempt to determine the mechanism by which this reaction occurs in order to deepen our understanding of how catalysis in metal-organic frameworks occurs.

1.1.2 Catalysis by Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are organic-inorganic crystalline hybrid materials with binding sites that can adsorb gas molecules. They have a porous, ordered structure comprised of inorganic clusters containing metal ions connected by organic ligands. They are useful in many applications, such as gas storage, gas separation, drug delivery, and more. They have especially been targeted for use in environmental applications, such as H$_2$ storage and CO$_2$ storage.

MOFs have properties ideal for the catalysis of chemical reactions. They perform heterogenous catalysis,
creating a lower-energy reaction pathway where the catalyst and the products and reactants are in different phases. Heterogenous reactions conveniently allow the products and reactants to be easily separated from the catalyst. Metal organic frameworks also have high internal surface area due to their porosity, which means that there is no volume inaccessible for catalysis, and can contain a high concentration of catalytic sites [2].

MOFs are similar to zeolites, inorganic mesoporous materials that are known to be the most important class of industrial heterogeneous catalysts [2]. However, one advantage MOFs have over zeolites is their tunability - they are known as the chemists’ “tinker toy.” The organic linkers and metal ions can be exchanged with similar ones to alter the properties of the MOF such as surface area, binding energy, or pore size. Changing these elements also affects the ability of the MOF to perform catalysis. MOFs can therefore be used for size-, shape-, and enantio-selective catalysis [3]. Understanding what properties of the MOF drive the catalysis of HD could guide the development of future MOFs for targeted catalysis.

1.2 Background

1.2.1 H\textsubscript{2}, D\textsubscript{2}, and HD

Hydrogen gas is made up of two hydrogen atoms bonded to one another. The nucleus of a hydrogen atom is a single proton. Deuterium gas is made up of two deuterium atoms bonded to one another. Deuterium is an isotope of hydrogen with a nucleus comprised of one proton and one neutron. A molecule formed from one atom of hydrogen bonded to one atom of deuterium is known as hydrogen deuteride or deuterium hydride, which we refer to as HD. These three gases, H\textsubscript{2}, D\textsubscript{2}, and HD, are isotopologues, or molecules that only differ by containing different isotopes of their elements. They are also chemically identical, meaning they behave the same way in chemical reactions, which makes them difficult to distinguish between or separate. Their main difference is their masses - a hydrogen molecule has a mass of 2 amu, a deuterium molecule has a mass of 4 amu, and an HD molecule has a mass of 3 amu.

1.2.2 The Reaction

Theoretically, HD gas can be formed from simple reaction in which a H\textsubscript{2} molecule and a D\textsubscript{2} molecule exchange atoms, yielding two molecules of HD. The equilibration between H\textsubscript{2}, D\textsubscript{2} and HD has been studied since the sixties due to its apparent simplicity. In terms of thermodynamics, the enthalpy change for this reaction is almost zero, since the reactants and the products are nearly chemically identical. Therefore, at equilibrium where the forward and backward reactions occur at the same rate, this reaction (equation 1.1) should yield
a statistical mixture of 25% $H_2$, 25% $D_2$, and 50% HD.

$$H_2 + D_2 \rightleftharpoons 2\text{HD}$$ (1.1)

However, in terms of kinetics, the reaction is difficult due to the stability of the H-H bond and D-D bond. There is a large energy barrier, nearly insurmountable at room temperature, to the reaction occurring without a catalyst. This reaction has been theoretically analyzed by Wilson and Goddard [4], who concluded that without the presence of a catalyst, the reaction would have a minimum theoretical barrier height of $132 \pm 20$ kcal/mol, or $550 \pm 80$ kJ/mol, which is comparable to the bond enthalpy of an H-H bond (436.002(4) kJ/mol) or a D-D bond (443.546(4) kJ/mol) [1].

1.2.3 Reaction Kinetics

The rate of the reaction depends on the concentration of the reactants and the temperature. The rate changes with concentration according to the rate law, and for the reaction in equation (1) would be

$$\text{rate} = -\frac{d[H_2]}{dt} = -\frac{d[D_2]}{dt} = \frac{1}{2} \frac{d[\text{HD}]}{dt} = k[H_2]^a[D_2]^b$$ (1.2)

where $[x]$ is the concentration of species $x$, and $k$ is the temperature-dependent rate constant. The sum of the exponents, in this case $a + b$, is called the order of the reaction. Since $H_2$ and $D_2$ behave identically in this reaction, we expect $a = b$. However, in our experiments we found it easier to examine the reverse reaction, in which two HD molecules form one molecule of $H_2$ and one molecule of $D_2$:

$$2\text{HD} \rightleftharpoons H_2 + D_2$$ (1.3)

For the reaction in this direction, the rate law is

$$\text{rate} = -\frac{1}{2} \frac{d[\text{HD}]}{dt} = \frac{d[D_2]}{dt} = \frac{d[H_2]}{dt} = k[\text{HD}]^n$$ (1.4)

where $n$ is the order of the reaction.

The rate of reaction is determined by the rate-limiting step, or the “slow” step, that has the largest energy barrier. How the rate-limiting step depends on the concentration of the reactants determines the order of the reaction. A reaction is generally expected to be first order if the rate-limiting step only involves one reactant molecule (unimolecular), while it is expected to be second order if the rate-limiting step involves two reactant molecules (bimolecular). Most reactions are either first order and second order. From the ideal gas law, the
partial pressure of species $x$ is $P_x = [x]RT$ where $R$ is the gas constant and $T$ is the temperature in kelvin. Thus for a given temperature, the pressure of an ideal gas is directly proportional to the concentration.

The rate constant $k$ varies with temperature according to Arrhenius’ law,

$$ k = Ae^{-E_a/RT} $$

(1.5)

where $R$ is the gas constant, $T$ is the temperature in kelvin, $A$ is a frequency factor that is proportional to the frequency of collisions, and $E_a$ is the activation energy of the reaction. From this equation, the activation energy of a reaction can be found by finding the slope of the graph of $\ln k$ vs. $1/T$. The difference between the activation energies of the forward reaction (equation 1.1) and the reverse reaction (equation 1.3) is the enthalpy change for this reaction, which can be calculated by subtracting the sum of the bond dissociation energies of the bonds broken from the sum of the bond dissociation energies of the bonds formed. The enthalpy change essentially gives the difference in energy levels between the products and the reactants. In this reaction, the products and reactants are very similar since they are isotopologues, so the enthalpy change is very small (0.7 kJ/mol). Therefore, the energy barrier for the forward reaction should be very similar to that of the reverse reaction.

1.2.4 Reactions on Surfaces

The heterogeneously catalyzed HD formation reaction could occur through a mechanism analogous to a reaction on a surface. There are two main ways for a two molecules to react on a surface: the Langmuir-Hinshelwood mechanism and the Eley-Rideal mechanism [5][6].

1.2.4.1 Langmuir-Hinshelwood Mechanism

In the Langmuir-Hinshelwood mechanism, two molecules adsorb on neighboring sites and then react and form the product or products, which then desorb. For reactants $A$ and $B$ and surface sites $S$, this mechanism has this form

$$ A(g) + S(s) \rightleftharpoons AS(s) $$

(1.6)

$$ B(g) + S(s) \rightleftharpoons BS(s) $$

(1.7)

$$ AS(s) + BS(s) \rightarrow \text{products} $$

(1.8)

The rate law for this mechanism is
\[
\text{rate} = k C_S^2 \frac{K_1 K_2 [A][B]}{(1 + K_1 [A] + K_2 [B])^2} \tag{1.9}
\]

where \( k \) is the temperature-dependent rate constant, \( C_S \) is the number of active sites per meter squared, \( K_1 \) is the equilibrium constant for the adsorption of A onto S, and \( K_2 \) is the equilibrium constant for the adsorption of B onto S [7] [5].

### 1.2.4.2 Eley-Rideal Mechanism

In the Eley-Rideal mechanism, only one molecule adsorbs while the other reacts while still in the gas phase:

\[
\begin{align*}
A(g) + S(s) & \rightleftharpoons AS(s) & \text{(1.10)} \\
AS(s) + B(g) & \rightarrow \text{products} & \text{(1.11)}
\end{align*}
\]

In reality, mechanisms in between Langmuir-Hinshelwood and Eley-Rideal can occur, where a species is partially adsorbed when it reacts. The rate law for this mechanism is

\[
r = k C_S[B] \frac{K_1 [A]}{K_1 [A] + 1} \tag{1.12}
\]

where \( k \) is the temperature-dependent rate constant, \( C_S \) is the number of active sites per meter squared, and \( K_1 \) is the equilibrium constant for the adsorption of A onto S [7] [5].

### 1.2.5 Methods of HD formation

#### 1.2.5.1 Shock Tube Experiments

HD gas was first formed experimentally by Farkas and Farkas in 1935 using a shock tube method, where \( \text{H}_2 \) and \( \text{D}_2 \) are heated to very high temperatures in an inert gas [8]. They hypothesized that the \( \text{H}_2 \) or \( \text{D}_2 \) molecules dissociated in a fast step, and the rate-limiting step, was atomic H or D displacing an atom on a diatomic molecule:

\[
\text{H} + \text{D}_2 \rightleftharpoons \text{HD} + \text{D} \tag{1.13}
\]

Thirty years later, studies found that \( \text{H}_2 \) did not dissociate at an appreciable rate in shock tubes, making the Faraks mechanism unlikely. In the sixties, more shock tube reactions were performed in which \( \text{H}_2 \) and \( \text{D}_2 \) gas were diluted with Ar gas and then heated to temperatures around 1000 K. Many of these reactions
seemed to indicate that the energy barrier was only around 40 kJ/mol for this reaction, much lower than the theoretically predicted numbers around 500 kJ/mol [4]. Lifshitz et al. showed that these results must have been due to adsorbed atomic hydrogen in the system, since when they took extra precaution to clean the system, they did not see formation of HD gas below 2500 K [9].

1.2.5.2 Astronomical HD Formation

HD gas forms naturally in outer space. Rotationally excited HD has been detected from giant planets by the Infrared Space Observatory and in the interstellar medium through UV-observations [10], and emissions from HD have been detected by the long-wavelength detector on the Infrared Space Observatory [11]. The formation of HD in interstellar clouds is thought to occur on dust grains through a Langmuir-Hinshelwood mechanism, Eley-Rideal mechanism, or a “hot atom” mechanism in between. The reaction can occur at the cold temperatures in space because H₂, D₂, and HD molecules can be ionized by cosmic rays, and reactions between ions have a much lower activation energy [12]. Experiments have shown formation of HD to occur on very cold (15 K) graphite surfaces, thought to be analagous to dust grains [13].

1.2.5.3 Transition Metal Catalysis

HD gas has mainly been produced experimentally using transition metal catalysts. One method involves directing a beam of H₂ (or D₂) at high temperatures (1900 K) atoms at a cold metal surface (around 120 K) such as Ni, Cu, or Pt, which is covered in adsorbed D (or H) atoms [14]. This reaction is thought to occur through the Eley-Rideal mechanism, where a gas-phase H₂ or D₂ molecule reacts with an atomic H or D adsorbed on the surface. Gold nanoparticles have also been theoretically predicted to be able to catalyze the reaction at room temperature without excitation by visible light through an Eley-Rideal mechanism when supported by a zeolite framework [15].

All the reaction methods discussed so far require a high energy input, either through radiation or high temperatures. However, the reaction proceeds at room temperature and even at liquid nitrogen temperature (78 K) on the surfaces of transition metals such as W, Ni, and Pt [16] and transition metal oxides Cr₂O₃, NiO, and Co₂O₄ [17]. The mechanism is thought to be through an oxidative addition/reductive elimination mechanism [18], a Langmuir-Hinshelwood mechanism where atomic H and D becomes adsorbed on the metal through oxidative addition, H₂ molecules reacts with the metal such that the H-H bond is broken but two metal-H bonds are formed. The metal is oxidized since it gives up electrons to form the metal-H bonds. The same process happens with D₂ molecules at the same rate, since they are chemically identical to H₂. The reverse reaction of oxidative addition is reductive elimination, through which two atoms adsorbed on neighboring sites on the metal form a bond between each other and break the bonds to the metal, during
which the metal is reduced and a gas molecule is formed. If the two neighboring adsorbed atoms were H and D, the product is an HD molecule.

### 1.2.5.4 Paramagnetic Centers

There are two systems in which the catalysis occurs at low temperatures without accessible open-metal sites - silica gel containing aluminum impurities, and magnesium oxide powders. Activated samples of MgO catalyze the reaction at temperatures as low as 78 K with very low activation energies around 2 kcal/mol, or 8 kJ/mol. The proposed mechanism is that paramagnetic centers formed from defects on the surface of the crystal catalyze the reaction, rather than the metal center [19]. The defect is formed due to a missing metal ion, which leaves a triangular array of \( O^- \) ions called \( V_1 \). An OH\(^-\) ion adjacent to \( V_1 \) “adsorbs the deuterium molecule to form a quasi-sorbed Rideal-Eley transition state bringing about exchange” [19].

The Metal-organic framework we are working with, MOF-74, shares similarities with the activated MgO samples in that it contains a metal center bonded to oxygens. MOF-74 crystals may also have paramagnetic centers due to defects on their surface that could catalyze the HD formation reaction through a similar mechanism.

### 1.2.6 The M-MOF-74 Isostructural Series

A metal-organic framework, as stated previously, is a type of highly ordered metal-coordinated polymer. One great strength of metal-organic frameworks is the ability to create different variants by changing the metal ion and the organic linker. In this thesis we examine members of the isostructural M-MOF-74 series, a type of metal-organic framework first synthesized by Rosi, et al. in 2005 [20] with hexagonal pores connected by helical rods (Figure 1.1). It has also been referred to as M2(dhtp), M/DOBDC, and M-CPO-27 [21]. The M refers to the identity of the metal in the structure: MOF-74 can be synthesized with Zn, Ni, Fe, Mn, Mg, Co, or Cu metal ions. MOF-74 crystals are made up of metal oxide clusters connected by organic ligands, or linkers, containing rigid benzene rings, which provide structure.

A metal ion in this structure is in the 2+ oxidation state, with a coordination number of six, meaning that it can be bonded to a maximum of six different groups. In the MOF-74 structure, it is bonded to five organic linkers, and therefore has the capability to bond to one more group. This is referred to as a coordinatively unsaturated metal site (CuS), or an open metal site. During synthesis, the metal centers are fully coordinated - the spots not attached to organic linkers are occupied by labile ligands, usually solvent molecules. They are removed by an activation step, where the MOF is heated for a long period of time under vacuum. This treatment causes the ligands to desorb, creating the coordinately unsaturated metal
Variants of M-MOF-74 were being studied for their ability to adsorb H2 and D2 for hydrogen storage and H2-D2 separation applications when its catalysis of the formation of HD gas from D2 and H2 was discovered. The two MOFs studied here are Co-MOF-74 and expanded Ni-MOF-74.

1.2.6.1 Co-MOF-74 (dodbc) and expanded Ni-MOF-74 (dobpdc)

Co-MOF-74 (dodbc) has the chemical formula Co$_2$C$_8$H$_2$O$_6$, often written as Co$_2$(dobdc) where dodbc is the organic linker 2,5-dioxido-1,4-benzenedicarboxylate, an aromatic ring with two carboxylate groups. Its structure has been determined by powder X-ray diffraction and neutron diffraction experiments: It has the space group $\overline{R}3$, and hexagonal pores with diameters of approximately 15 Å. Each metal center has one open metal site, which is the primary binding site for gas adsorption. There are three more binding sites associated with the organic ligands [22].

Expanded versions of MOF-74 have been synthesized to test the effects of larger pores on the properties of the MOF. Expanded Ni MOF-74 has the chemical formula Ni$_2$(dobpdc). It shares the basic structure of the rest of the MOF-74 series, but has 4,4’-dioxidobiphenyl-3,3’-dicarboxylate (dobpdc) linkers instead of dodbc linkers, which contain two aromatic rings instead of one [23]. These longer linkers do not significantly change the pore shape, but lead to a larger pore volume.
Figure 1.2: Comparison of original MOF-74 organic ligand, dobdc, with the extended version used in the expanded MOF, dobpdc. The negatively charged oxygen atoms are where the ligand would bond to a metal ion, forming the oxide cluster.

1.2.6.2 Previous MOFs tested for catalysis

Co-MOF-74 (dodbc), Ni-MOF-74 (dodbc), Mg-MOF-74 (dodbc), and Ni-MOF-74 (m-dodbc) samples have been observed to catalyze the formation of HD from $\text{H}_2$ and $\text{D}_2$ gas either by mass spectrometry which we use here, or infrared spectroscopy, which can observe the vibrations of HD adsorbed on the MOF. Due to the lack of a dipole moment, $\text{H}_2$, $\text{D}_2$, and HD are only visible to IR when adsorbed on the MOF structure. Therefore, to be examined using IR spectroscopy, a gas mixture must be cooled down to at least liquid nitrogen temperature so the gases adsorb onto the MOF. Cooling down the sample also avoids broadening of the adsorption bands, which occurs at higher temperatures. Infrared spectra were taken using a geometry called diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) that can obtain the IR spectra of powder samples.

Testing for HD formation was done by cooling down a gas mixture of 50% $\text{H}_2$ and 50% $\text{D}_2$ to 30 K in the presence of the MOF powder, taking an initial IR spectrum, warming up the system to room temperature and leaving it overnight, and then cooling it down to 30 K again to take a final IR spectrum. After leaving the gases to react at room temperature, a peak at the frequency expected for adsorbed HD appeared, indicating HD had been formed (Figure 1.3).

The effect of exposure to air on the catalysis was also tested: the Co-MOF-74 sample appeared to not catalyze the reaction at an appreciable rate after being exposed to air, which presumably blocks the open metal sites with ligands such as water vapor, but then catalyzed the reaction once again when reactivated by heating at 180°C, as observed by mass spectrometry (Figure 1.4).
Figure 1.3: IR spectra of adsorbed gas showing HD formation Co-MOF-74. HD formation was examined with Diffuse Reflectance Fourier Transform Infrared Spectroscopy at 30 K before (blue line) and after (red line) exposing a gas mixture of 50% H$_2$ and 50% D$_2$ to a sample of Co-MOF-74 overnight at room temperature.

Figure 1.4: Formation of HD in Ni-MOF-74 before and after exposure to air seen by mass spectrometer. After initially activated at 200°C, the signal from HD increased relative to the total signal, indicating that HD was being formed. HD formation occurred much more slowly after exposure to air (blue dot), but was observed once again at a faster rate after the Ni-MOF-74 sample was reactivated at 180°C (open circle).
1.2.7 MOFs as Catalysts

There are three main ways in which people use metal-organic frameworks to catalyze chemical reactions. They differ by the location of the active site, or where the reaction takes place.

The first method of MOF catalysis involves using the metal centers in the MOF structure itself as active sites. Substrates can bond to the metal ions in positions not occupied by the lattice [24], and the high concentration of metal centers in a MOF makes it advantageous to use them as active sites. For example, if the metal in the MOF is coordinately unsaturated, it can behave as a Lewis acid, forming metal-ligand bonds by accepting electrons from electron-rich ligands such as cyanide. The metal organic framework HKUST-1 has been used to perform cyanosilylation of benzaldehyde or acetone [3]. Structural defects in MOFs can also intentionally be used as active sites for catalysis [25].

In the second method, the organic ligands or linkers between the metal nodes can be used as active sites.

In the third method, the MOF serves a structural support for a guest species that occupies the MOF’s pores. MOFs have been used as supports for metal nanoparticles that catalyze reactions [24]. For example, nickel nanoparticles supported by MOFs have been shown to catalyze the hydrogenation of nitrobenzene [26].

1.2.8 Possible Mechanisms for MOF Catalysis of HD formation

It has been shown previously that the reaction happens on an appreciable timescale in the presence of a MOF-74 sample, and does not otherwise. However, it is unclear whether the MOF structure itself is catalyzing the reaction, or whether the MOF sample contains impurities that catalyze the reaction.

There could be small metal particles not incorporated into the MOF framework left over from the synthesis of the MOF. These particles could act like the nanoparticles supported by a MOF framework, and form HD through an oxidative addition reductive elimination mechanism. However, it would be difficult to detect unincorporated metal particles, since they are most likely the same metal that is incorporated into the MOF.

Another possibility is that the metal node in the MOF structure is performing the reaction. However, this pathway seems unlikely due to the lack of two open-metal sites, which would not allow gas molecules or atomic H or D to adsorb onto neighboring sites and form HD through a Langmuir-Hinshelwood mechanism. An Eley-Rideal mechanism also seems unlikely, because with only one open-metal site, oxidative addition cannot occur, so atomic H or D cannot be adsorbed on the metal, and when a gas molecule bound to an open-metal site, its bond strength is only weakened a few percent, so a significant amount of energy would still be required to break the H-H or D-D bond.

The third possibility is that the catalyst sites in the MOF are paramagnetic centers, perhaps at defects.
on the surface of the MOF crystals, as in the case of catalysis by MgO. This possibility does not require
the MOF centers to be involved, so it is not an issue that the metals in the MOF structure do not have
enough open-metal sites. However, it appears to not have been studied previously in the MOF literature.
The goal of this research was to take preliminary steps to understand this reaction and find clues as to the
mechanism by which it occurs. We investigated the dependence of the rate of the reaction on temperature
and concentration.
Chapter 2

Experimental Apparatus and Procedure

2.1 Experimental Setup

We used the Micromeritics ASAP 2020, a computer controlled machine for dosing the system with a known amount of particular gas at a particular pressure. The ASAP (Accelerated Surface Area and Porosimetry) system contains solenoid valves that can be digitally controlled by computer software to load and evacuate gases. The pressure is monitored by a high pressure (10 to 1000 mbar) and low pressure (1 to 10 mbar) gauges, and can be evacuated using a turbomolecular pump. The system also contains a heating mantle for degassing. The ASAP system is connected by Swagelok connectors and copper tubing to a T junction. One path leads to the sample held in a glass bulb, and the other to the detector, a quadrupole mass spectrometer (Figure 2.1).

2.1.1 Mass Spectrometer

The concentrations of $\text{H}_2$, $\text{D}_2$, and HD were monitored over the course of the reaction using a Hiden “Lo-MASS” series quadrupole mass spectrometer (QMS) specialized for distinguishing low-mass species and quantifying gas mixtures [28]. Unlike in tandem mass spectrometry, there is no collision cell, and all three quadrupoles are used as mass filters, giving it higher sensitivity and long-term stability [29]. Our model has two available detectors: a Faraday cup to analyze higher pressures of gas, and a secondary electron multiplier (SEM) for sensitivity to low concentrations of gas.

The operating pressure of the mass spectrometer is on the order of $10^{-9}$ Torr, much less than the pressure of the rest of the system. The mass spectrometer therefore samples the gas mixture through a capillary that limits the flow of gas into the mass spectrometer. We used the “low flow” capillary that limits the flow in
Figure 2.1: Block diagram of experimental apparatus. The Accelerated Surface Area and Porosimetry System (ASAP) is used to load a known amount of gas into the system at a certain pressure. The gas is then exposed to the MOF sample in a long-necked glass bulb. Gas in the line is sampled by the capillary of the quadrupole mass spectrometer (QMS), which detects the different concentrations of gases. The volume of (a) the dosing volume is ~64 cm³, (b) the tubing is ~10 cm³, and (c) the sample holder is ~27 cm³.

Figure 2.2: Schematic of triple mass filter quadrupole mass spectrometer, modified from [27]. Gas molecules from the inlet are turned into ions by electron ionization. Ions with the selected mass-to-charge ratio travel through the three quadrupoles to the detector, while the others are deflected. The ions are then detected by a secondary electron multiplier detector.
order to minimize the effect of the mass spectrometer sampling on the system. After moving through the inlet, the gas molecules are ionized through electron ionization: 70 eV electrons bombard the molecules, which causes them to ionize, producing positive ions [30]. These ions are sorted by mass-to-charge ratio (m/z) by the quadrupole mass analyzer. Each quadrupole is made up of four metal rods with an electric field tuned such that only ions with a certain m/z pass through, and the rest are deflected. The ions travel through three of these mass filters in series. The particles with the selected m/z then reach the detector, in our case a secondary electron multiplier (SEM). The SEM uses secondary electron emission: the ions strike a metal cathode, expelling secondary electrons which are then multiplied using a continuous dynode and converted into a digital signal.

Which m/z values to scan for are selected through the MASsoft 7 Professional software. The mass spectrometer then cycles between scanning for each of the selected ions in cycles of around 15 seconds. The signal from the mass spectrometer from each cycle is transmitted back to the computer, which records the signal from each mass-to-charge ratio and plots the signals over time using MASsoft 7 (see Figure 2.3).

The sensitivity of the detector is not the same for all species. Figure 2.4 shows that the signal produced by a given pressure of H₂ in the system is much larger than the signal for the same pressure of D₂ gas. The overall differences in sensitivity for different species, called the overall sensitivity factor (RSF), is due to a combination of effects from the inlet, the sensitivity of the source, the fragmentation, the quadrupole transmission, and the detection efficiency. For small low molecular weight gases such as H₂, D₂, and HD, the probability of fragmentation is very low and can be ignored. The largest effect is how quickly the gases pass through the inlet - the speed of the gas roughly follows a $M^{-1}$ law, since particles with larger masses travel more slowly through the inlet capillary.

Therefore, for the gases we are considering, relative sensitivity should scale inversely with molecular mass. As a result, the signals produced by two species, both at the same concentration, are not necessarily the same: the H₂ signal is expected to be around twice that of D₂ [30], and around 3/2 that of HD. Results for the relative sensitivities of H₂ compared with He, which has the same molecular mass as D₂, give a ratio of signals for H₂/D₂ of 2.8, approximately the same as we found experimentally.

The ionization process can shift the signal by creating a background signal that is not proportional to the concentration of the species in the system. The fragmentation of H₂O molecules in the system from the water vapor in the air can create H₃⁺ ions, which are then detected as H₂, even though they originated from gaseous H₂O and not H₂ gas. This effect leads to a slowly increasing background level of H₂ due to water vapor in the system. Additionally, H₂ and D₂ gases may fragment and produce atomic hydrogen and deuterium ions, which could combine to form HD inside of the mass spectrometer. This effect produces a low HD background signal present even when no HD is in the system.
2.1.2 Synthesis of MOF Samples

Samples of Co-MOF-74 and expanded Ni-MOF-74 were synthesized by Jeffrey Long’s group at the University of California at Berkeley. The Co-MOF-74 sample, more formally Co$_2$(dobdc), was synthesized by combining H$_4$(dobdc) with the metal complex Co(NO$_3$)$_2$ · 6H2O in a 1:1:1 mixture of DMF/ethanol/water in a sealed jar, and then sonicating the reactants until they dissolved. The solution was then heated in an oven at 100°C. The resulting crystals were then soaked in DMF for 24 hours at 120 °C and then in methanol at 60 °C [31]. The expanded Ni-MOF-74 sample, or Ni$_2$(dobpdc), was synthesized similarly, through the combination of H$_4$(dobpdc) with a divalent nickel salts under solvothermal conditions using an alcohol/amide solvent mixture [23].

The expanded Ni-MOF-74 sample was tested first. 57.4 mg of powder were weighed out and inserted into the sample holder, a ~30 cm$^3$ long-necked glass bulb, in a glove box under an argon atmosphere. We then tested a MOF sample with nearly an order of magnitude more powder in hopes of collecting data more quickly due to a faster rate. A sample of 941 mg of Co-MOF–74 was weighed out and inserted into an identical glass bulb in the same glove box. Later, a 70.4 mg sample of Co-MOF-74 was also weighted out and experimented on.

2.2 Development of Procedure

The first goal was to observe how fast the reaction progressed at room temperature and how the rate of the reaction changed over time. The most straightforward way to do this would be to load equal amounts of H$_2$ and D$_2$ gas and monitor the signals produced by H$_2$, D$_2$, and HD continuously to observe the rate at which H$_2$ and D$_2$ are consumed and HD is formed.

However, the sampling of the system by the mass spectrometer affects the system - even using a low flow-through capillary, the pressure in the system decreases significantly due to gas flowing into the mass spectrometer, especially at high pressures. To deal with this issue, we opened the valve to the capillary of the mass spectrometer periodically for small periods of time (around one to two minutes) to minimize the pressure change, and analyzed the ratio of the signals rather than the absolute signals to get a measure of the reaction progress independent of the changing total pressure. This should work because the gases should all be sampled by the mass spectrometer proportionally to their concentrations/partial pressures.

At first, we attempted to make gas mixture of 50% H$_2$ and 50% D$_2$ and observe the production of HD gas in the forward direction (equation 1). A 150 cm$^3$ cylinder was loaded with H$_2$, and the volume inside the ASAP system was loaded with the same number of molecules of D$_2$. They were then allowed to mix in
the line before being exposed to the MOF sample. However, it was found that even after an hour the gases were not fully mixed. The mass spectrometer signal did not show a 1:1 ratio between the H₂ and D₂ signals, even when corrected for relative sensitivity factors.

Then the reaction was run in the reverse direction, starting with only HD, in which HD is “scrambled” to produce equimolar amounts of H₂ and D₂:

\[
2 \text{HD} \rightarrow \text{H}_2 + \text{D}_2
\]  

(2.1)

Since only pure HD is loaded, there is no mixing necessary, and the reaction is guaranteed to produce a 1:1 ratio of H₂ and D₂. Originally a metal sample holder with a volume of only around 1 cm³ was used, but it was switched out for an approximately 30 cm³ glass bulb to increase the volume of gas around the MOF sample relative to the gas in the rest of the system, increasing the rate of catalysis. There was one issue encountered when loading HD: usually the valves to the cylinders are left open, and gases from the cylinders are stored in the line from the cylinder to the ASAP machine in addition to in the cylinder. However, replacing the regular on the cylinder of HD gas, gas that was left in the line from the HD cylinder to the ASAP machine overnight had much lower purity than usual - a HD/D₂ ratio of around 28 rather than the ratio of about 80 seen consistently in previous runs. From that point onward we evacuated the HD line and used HD gas fresh from the cylinder for all runs.

### 2.3 Data Collection

Because of the changing pressure in the experiments, we examined the ratio of the signal produced by HD to the signal produced by D₂ from the mass spectrometer. The concentrations of H₂ and D₂ produced by the reaction should be identical, but we chose to use D₂ in our calculations due to the much lower background level of D₂ relative to H₂, since H₂ background is generated by traces of water vapor in the mass spectrometer. The ratio of the HD signal to the D₂ signal was used as a measure of reaction progress. The ratio decreases over time, as HD is consumed and D₂ is formed during the reaction.

We investigated both how the rate of the reaction changed over time as the reaction progressed at various temperatures to determine the activation energy \( E_a \) for each of the samples, and how much reaction progressed after a fixed amount of time (30 minutes) at varying total pressures to try to determine the order of the rate law for this reaction.
Figure 2.3: Example of trace from Mass Spectrometer, expanded Ni-MOF-74 at 348 K (75°C). The vertical axis is the mass spectrometer signal in arbitrary units. The peaks in the signal occur when MS valve was opened. The clear decrease in HD signal is caused by pressure decrease due to the mass spectrometer.
2.3.1 Varying Temperature

For the expanded Ni-MOF-74 sample, around 250 mbar of HD was loaded into the system and exposed to the sample at 273 K (0°C), 296 K (23°C), 318 K (45°C), 348 K (75°C), and 398 K (125°C). At lower temperatures, the reaction would most likely not occur at an appreciable rate, and higher temperatures risk damaging the MOF sample. To obtain the desired temperature, the sample was either cooled in an ice-water bath, heated in a heating mantle, or left at room temperature. For the runs above room temperature, the temperature of the mantle was maintained at a constant, set value using a thermocouple.

At a given temperature, the reaction was monitored with mass spectrometry. To reduce the loss of pressure due to the mass spectrometer, the MS valve was opened for short periods of one to two minutes. The MS valve was opened to record signals produced by H₂, HD, and D₂ in the gas mixture at first every 10 minutes, and then every 20 minutes, and then at longer intervals as the rate of reaction decreased due to the system approaching equilibrium. An example of a trace from the MasSoft program is given in Figure 2.3.

Data were taken initially over a period of three to six hours, and then the gas below the T valve (see Figure 2.1) was saved and left to react overnight and then sampled with the mass spectrometer the day after. The HD/D₂ ratio overall decreased throughout the run at all temperatures tested from 273 K to 398 K, indicating that the reaction was progressing and thus being catalyzed by the MOF sample.

For the Co-MOF-74 sample, the same procedure was used but a higher initial pressure of around 500 mbar of HD was loaded into the system due to acquiring a new cylinder of HD gas. The purity of this HD gas was higher than previously, so the initial HD/D₂ pressure ratio for these runs was higher than those done with the expanded Ni-MOF-74 sample. The experiment was run at 296 K (23°C), 318 K (45°C), 348 K (75°C), and 396 K (125°C). For this sample, a run was not conducted at 273 K since we predicted the reaction would have been too slow to observe on a reasonable timescale. Once again, the HD/D₂ ratio overall decreased throughout the run at all temperatures tested from 273 K to 398 K, indicating that the reaction was progressing and the catalysis was occurring.

However, heating appeared to affect the reaction. After maintaining the Co-MOF-74 powder at 398 K (125°C) overnight and then cooling the sample holder and the mantle to room temperature, the reaction preceded more quickly than previously observed at room temperature - the HD/D₂ signal ratio decreased much more quickly, indicating that HD was being consumed and D₂ was being produced more quickly. This effect was discovered to be caused by the sample not fully cooling rather than the sample being activated by heating (see results section). This issue could be mitigated by waiting longer for the sample to cool and filling the sample holder with He gas while cooling.
2.3.2 Varying Initial Pressure

Pressure of the gas initially loaded was varied from around 10 mbar to around 300 mbar. First the mass spectrometer valve was opened for around 90 seconds to determine the HD/D$_2$ ratio for the unreacted gas, and then the gas was exposed to the MOF sample kept at a constant temperature of 125°C, causing a drop in pressure as the gas flowed into the evacuated sample holder. The pressure was recorded after it dropped to the pressure at which the reaction would occur. The mass spectrometer valve was then reopened after around 30 minutes, and data were collected. Both the expanded Ni-MOF-74 and the Co-MOF-74 samples were tested at five different pressures, ranging from 10 mbar to 400 mbar.

2.3.3 Calibration of the Mass Spectrometer Signal

The mass spectrometer signal should be proportional to the concentration and the pressure of the gas in the system. However, at lower pressures the relationship between the signal and pressure becomes nonlinear. To quantify how the mass spectrometer signal varied with the pressure of the gas, we loaded a known pressure of pure gas (either H$_2$, D$_2$, or HD) into the system with the T valve closed (so the gas is not exposed to the MOF sample). The initial pressure was recorded, then the MS valve was opened for one to two minutes. The initial (maximum) signal and the final signal right before closing the valve were recorded. Plotting the
average of the initial and final signals versus the average of the initial and final pressures yielded calibration curves used to convert the mass spectrometer signals to pressures of each species (Figure 2.4).
Chapter 3

Results and Analysis

3.1 Calibration of Mass Spectrometer Signal

The mass spectrometer produces a signal in arbitrary units. We define $10^{-10}$ of the units given by the MasSoft 7 software to be a mass spectrometer unit (msu). The mass spectrometer signal was found to vary linearly with the pressure at pressures at or above around 100 mbar, but the relationship appears more quadratic at pressures below 100 mbar for $\text{H}_2$, $\text{D}_2$, and $\text{H}\text{D}$.

The low pressure region of the $\text{D}_2$ and the HD calibration curve (pressures less than 100 mbar) were fit to a second-degree polynomial with the $y$-intercept set to 0 (Figure 3.1, Figure 3.2) in order to convert the mass spectrometer signals. The high pressure region of the HD calibration curve (pressures greater than 100 mbar) was fit to a line (Figure 3.3). The fits were unweighted, and the equations generated from these fits are not based on physical models: the equations were found in order to calculate physically significant pressure values from the signals produced by the mass spectrometer for $\text{H}_2$, $\text{D}_2$, and HD. At the boundary between the linear and quadratic regions, the fit equations give similar results. For example, for a $\text{D}_2$ signal of 300 msu, the linear curve gives 107 mbar and the quadratic curve gives 115 mbar.

3.2 Estimating Activation Energy

The rate of the reaction increased with temperature, as expected. At higher temperatures, $\text{HD}/\text{D}_2$ ratio versus time curves had larger, more negative slopes that more quickly leveled off than at lower temperatures. The initial slopes of the graphs (a weighted linear fit to the first three points of each run) were used to find a rough estimate of the activation energy for the reaction. We plotted the natural logarithm of the absolute
Figure 3.1: $\text{D}_2$ calibration curve used to calculate $\text{D}_2$ partial pressures from mass spectrometer signals. The low pressure region of the $\text{D}_2$ calibration curve was fit to a second-degree polynomial, yielding the equation $y = 0.0173x^2 + 0.618x$, where $x$ is the pressure in mbar and $y$ is the signal from $\text{D}_2$ in msu.

Figure 3.2: HD calibration curve used to convert HD partial pressures from mass spectrometer signals. The low pressure region of the HD calibration curve was fit to a second-degree polynomial, yielding the equation $y = (2.7 \times 10^{-5})x^2 + 0.011x$, where $x$ is the HD partial pressure in mbar and $y$ is the signal from HD in msu.
Figure 3.3: HD calibration curve used to convert HD partial pressures from mass spectrometer signals. The high pressure region of the curve was fit to a line, yielding the equation \( y = 8.6x - 5.3 \), where \( y \) is the MS signal for HD in msu, and \( x \) is the pressure of HD in mbar.

Value of the slopes versus the reciprocal of the temperature, performed a weighted linear regression, and estimated the activation energy of the reaction \( E_a \) from the slope of this line according to

\[
\ln k = -E_a \left( \frac{1}{RT} \right) + \ln A,
\]

where the gas constant \( R = 8.314 \times 10^{-3} \text{ kJ/mol} \). We found the activation energy to be \( 7 \pm 2 \text{ kJ/mol} \) for the expanded Ni-MOF-74 sample and \( 7 \pm 8 \text{ kJ/mol} \) for the Co-MOF-74 (Figure 3.5).

3.2.1 Issues with Determining Temperature

We assumed that the sample in the glass sample holder was the same temperature as the heating mantle when determining the activation energy. This assumption may have been incorrect, especially for the much larger amount of Co-MOF-74 tested. This effect may be due to the much greater amount of sample in the sample holder leading to difficulty in heating the parts of the sample in the middle. In addition, MOFs are poor thermal conductors due to their porous nature, and they are generally cooled under vacuum, which means that there is not a significant amount of gas flowing through the sample to cool it by convection. To deal with this issue, while cooling the sample we filled the sample holder with helium.
Figure 3.4: Reaction of HD to form $H_2$ and $D_2$ over time at varying temperatures in (a) expanded Ni-MOF-74 and (b) Co-MOF-74 samples. The reaction progress is represented by the ratio of the partial pressure of HD to that of $D_2$. $H_2$ was not used due to the varying background signal seen on the mass spectrometer.
Figure 3.5: Estimation of Activation Energy for Expanded Ni-MOF-74 (a) and Co-MOF-74 (b) by linear regression on plot of \( \ln k \) vs. \( 1/(RT) \).
3.3 Determining Reaction Order

We expect the rate-limiting step in the reaction to be either unimolecular (only one reactant molecule is involved) or bimolecular (two reactant molecules are involved). For either a first-order or second-order reaction, the rate is expected to increase with a higher initial pressure of HD gas. We measured the rate at different pressures by measuring how much the D₂ gas was formed in 30 minutes at varying pressures pressures at a fixed temperature of 398 K (125°C). The D₂ signals before and after the reaction were converted to pressures using the fit to the D₂ curve in Figure 3.1 to compute the change in the partial pressure of D₂. The change in the partial pressure of D₂ was then plotted versus the total pressure to show the relationship between the rate of the reaction and the pressure of the system (Figure 3.6).

Since the increase in D₂ partial pressure in 30 minutes is proportional to the average rate of the reaction over that period, and the total pressure is proportional to the concentration, this graph gives information about the order of the rate of the reaction (see Reaction Kinetics section). For all samples, the relationship between rate and concentration appears closer to linear than quadratic (Figure 3.6). This result indicates that the reaction is more likely to be first order than second order, i.e. the rate-limiting step of the reaction may be unimolecular. Additionally, the 70 mg expanded Ni-MOF-74 sample and the 940 mg Co-MOF-74 sample strangely showed a very similar relationship between pressure and reaction rate where the rate levels off at higher system pressures, while for the 70 mg Co-MOF-74 sample the rate appears to increase linearly over the whole range of pressures tested. At and above 150 mbar, it appears that the reaction progresses faster in the 70 mg sample of Co-MOF-74 than in the 940-mg sample, which seems incredibly unlikely, so the data from these runs is suspect. The procedure used to conduct these runs may be less reliable than the procedure used to compare the rate of the reaction at different temperatures, since the valve to the 40 cm³ loading volume has to be left open to get accurate measure of the initial partial pressure of D₂, and there is greater space for D₂ gas to flow into where it cannot be sampled by the mass spectrometer. However, this effect would not explain the reaction progressing faster for a smaller amount of MOF. A more likely explanation is that the much larger sample of Co-MOF-74 powder had not reached 398 K, so it was in fact at a lower temperature than the runs done with the smaller sample of Co-MOF-74.
3.4 Reproducibility

The data from experiments observing the HD/D₂ ratio over time at a given pressure appear consistent and reproducible. Experimental runs performed at room temperature (296 K) with the Co-MOF-74 sample performed weeks apart were found to be nearly identical. Between these two runs, different runs were performed at other temperatures with the same sample, the sample was heated under vacuum for a couple of hours at 140°C and then the next day for a few hours at 150°C in an attempt to further activate the sample, and the sample holder was left overnight filled with a gas mixture at 125°C. After filling the sample holder with helium and letting the sample cool to room temperature overnight, the sample appeared to return to its previous state in terms of its ability to catalyze the reaction at room temperature (Figure 3.7).

3.5 Discussion

Here are the facts we have obtained about the MOF-catalyzed conversion of HD into H₂ and D₂: the reaction has occurred observably at room temperature in a sample of expanded Ni-MOF-74 and a sample of Co-MOF-74. The reaction progresses faster at higher temperatures, as measured by the rate of decrease in the HD/D₂ ratio. The reaction occurs faster at higher total pressures, as measured by the production of D₂ gas, and has an activation energy on the order of 7 kJ/mol for both samples. Additionally, the rate of
Figure 3.7: Two experimental runs at 296 K (23°C) with Co-MOF-74 sample. The “before” run was done with less pure HD, so was shifted horizontally by 27 minutes relative to the “after” run.

The reaction appears to increase roughly linearly with concentration (Figure 3.6). From these preliminary data, we cannot definitively conclude any more; however, we can speculate about the mechanism that may be occurring.

The activation energies of both the expanded Ni-MOF-74 and the Co-MOF-74 samples obtained are identical, and both samples appear to have the same dependence of the rate on concentration. These results suggest that catalysis in both expanded Ni-MOF-74 and Co-MOF-74 occur by the same mechanism. Since the main structural difference between these two MOF samples is the length of the linkers, this result hints that the linkers have a negligible effect on the catalysis. Understanding the effect of the identity of the metal in the MOF structure requires further experiment. Additionally, the activation energies for this reaction agree with those of HD formation in activated MgO powders with proton impurities, 8 kJ/mol [19].
Chapter 4

Conclusions and Future Work

4.1 Conclusions

In this thesis, the reaction converting HD into H$_2$ and D$_2$ in the presence of a metal-organic framework was explored. A triple-filter mass spectrometer was used to monitor the partial pressures of H$_2$, D$_2$, and HD as the reaction progressed. Gas from the reaction mixture was only allowed to enter the mass spectrometer intermittently to reduce gas loss; however, the pressure in the system still decreased significantly throughout the runs.

We found that the reaction occurred appreciably in a 57.4 mg sample of expanded Ni-MOF-74 at 273 K, 296 K, 318 K, 348 K, and 396 K with an initial pressure of around 250 mbar of HD gas, and in a 941 mg sample of Co-MOF-74 at 296 K, 318 K, 348 K, and 396 K with an initial pressure of around 500 mbar of HD gas. We observed the activation energy to be on the order of 10 kJ/mol, significantly lower than the uncatalyzed energy barrier on the order of 500 kJ/mol. Additionally, there was a roughly linear relationship between reaction rate and total pressure. From these preliminary data, we speculate that the reaction may be catalyzed by paramagnetic centers created by defects on the surfaces of MOF crystals, since the activation energy was identical to that of MgO. In conclusion, we consistently found HD gas to react to form H$_2$ and D$_2$ in two different MOF-74 samples, demonstrating that the HD formation seen previously was a real effect, and have obtained estimates of the activation energy and the reaction order.
4.2 Future Work

4.2.1 Experimental Apparatus Improvements

Our quadrupole mass spectrometer was designed to be used with a flow-through system, in which the reactant gas flows at a constant rate across the sample, the pressure stays constant, and the rate of formation of HD or H₂ and D₂ is measured. Changing the design of our experimental apparatus to this sort of system would negate the issues with changing volume due to the sampling of the mass spectrometer, which is designed. If that is not feasible, automating the periodic opening and closing of the valve to the mass spectrometer to take data points by using a solenoid valve, controlled by an interval timer or LabView program, would make data collection much more convenient and consistent.

4.2.2 Future Experiments

There are many factors that could affect the rate of the reaction to investigate that could help us to understand how the catalysis occurs. Further experiments we are planning using Co-MOF-74 include testing different amounts of MOF sample to investigate how the number of accessible active sites scale with the mass of MOF, and whether the catalysis is occurring due to the MOF itself, or impurities in the MOF. Repeating the experiment done previously where we measuring the catalytic activity of the MOF, expose it to air, and then measure the catalytic activity again could also give information about what sort of active site catalyzes the reaction. A better determination of the rate law could be achieved by increasing the range of pressures studied.

Studying other variants of MOF-74 or other types of MOFs could give information about what aspects of the MOF affect whether the catalysis of the reaction occurs, and its rate. Comparing Mg-MOF-74 to Zn-MOF-74 would be especially interesting, since Mg and Zn are the farthest apart on the periodic table of all the metals that MOF-74 can be made with. Characterization of the MOF samples to look for paramagnetic centers or residual metal particles could yield information important to determining the possible mechanism.
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Bibliography


[29] Mass spectrometers for residual gas analysis - RGA: For applications in a vacuum environment [powerpoint slides].
