CHEMICAL HEAT PUMP BASED ON HEMIAMINAL REVERSIBLE REACTIONS

by

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Heat pumps are widely used in different fields, such as the petroleum and chemical industries, brewery, printing, etc. Traditional heat pump based on lithium bromide-water or ammonia-water as refrigerant and absorber waste a lot of energy while using it to absorb heat from the environment. The low efficiency of traditional heat pump is an obstacle for development. In recent years, chemical heat pumps based on reversible chemical reactions were introduced, which can improve the efficiency and have a great potential. The hemiaminal reaction, which is one of the chemical reactions, can be potentially used in chemical heat pump based on reversible chemical reactions. In this paper, simulations of hemiaminal reactions and simulated process design of heat pump based on hemiaminal reaction is discussed. Two ways were used to calculate the equilibrium constant of hemiaminal reaction: 1) density functional theory(DFT) and 2) neural network (NN). And based on the simulated equilibrium constant, the whole process was simulated in Aspen Plus and simulation result shows the new chemical heat pump system can get a coefficient of performance (COP) more than 2.5, which is higher than the literature results of other kind of chemical heat pump (between 1.0 to 2.4 [17]). There is a great possibility that, in the future, this kind of chemical heat pump will be widely used in different fields.

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PREFACE

I would first like to thank my thesis advisor Professor Eric J. Beckman of Department of Chemical and Petroleum Engineering at University of Pittsburgh. The door of Professor Beckman office was always open whenever I ran into a trouble spot about my research and writing. He consistently allowed this thesis paper to be my own work, but steered me in the right the direction whenever he thought I needed it.

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Finally, I much express my very profound gratitude to my parents for providing me with unfailing support and continuous encouragement throughout my two years of study in the United States. This accomplishment would not have been possible without them. Thank you very much.

Xin Su

1.0 INTRODUCTION

1.1 TRADITIONAL HEAT PUMP

A heat pump is a technology that can transfer heat from a low temperature environment to a high temperature environment. [1] Heat pump is a device designed to move heat in the opposite way of normal heat flow, which is releasing heat from a warmer body to a cold body. Heat pump takes heat from a cold space and releases it to a warmer one. Based on the Clausius statement of the Second Law of Thermodynamics, it is clearly that such heat transfer requires a heat input or work input: [2]

"It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body."

Thus it is clear that heat pump needs a certain amount of work to transfer heat from a lower temperature space to a higher one.

In 1857, Peter Von Rittinger first developed and built heat pump, [3] and after more than one hundred years' development, heat pump can be generally divided and classified into three different types: traditional vapor compression heat pump, [4,5] adsorption heat pump [6-8] and chemical heat pump [9-11]. Generally speaking, vapor compression heat pump is the most widely used among these three different types. In the past decades, almost every refrigerator used vapor compression heat pump which contains Chlorofluorocarbons (CFC) [6]. However, CFC has been proved that it depletes the ozone layer and can cause environment problems. Hydrofluorocarbon (HFC), which has similar thermodynamic properties compared with CFC, can be a good replacement using in the vapor compression heat pump [37]. However, Scientists have shown that even though HFC will not deplete ozone layer, it will cause a severe greenhouse problem. In recent years, because of these environment problems generated by vapor compression heat pump, more and more research focused on absorption heat pump and chemical heat pump.

1.1.1 Working principle of heat pump

The basic principle of a traditional heat pump is to use different boiling points of a fluid depending on the pressure. By lowing the pressure, a medium can be evaporated at low temperature. Evaporation process will absorb heat from low temperature space. While the pressure increases, the medium after evaporation will be condensed at high temperature, and condensation will release heat from the medium to the high temperature environment. [12] That is how heat pump transfer heat from lower temperature body to higher temperature one. It is a closed circuit thus the medium can be recycled and the heat is transported and transferred by the medium.

1.1.2 Performance of heat pump

Scientists and engineers use the coefficient of performance (COP) to represent the performance of efficiency of a heat pump. Basically, COP is a ratio of heat delivered per work input. [13] In general, higher COP means better performance. The basic equation of COP can be written in the following way:

$$COP = {}^{Q}/_{W} \qquad \text{Equation 1-1}$$

where Q is useful heat from the system, and W is the work or heat input required by the system. In a reversible heat pump system, according to the First Law of Thermodynamics, it has equations:

$$Q_{hot} = Q_{cold} + W \qquad \text{Equation 1-2}$$

$$\mathrm{W} = Q_{hot} - Q_{cold} \qquad \text{Equation 1-3}$$

where Q_{hot} is the heat released to hot space and Q_{cold} is the heat suck from the cold space.

Therefore, based on equations above,

$$COP_{heating} = \frac{Q_{hot}}{Q_{hot} - Q_{cold}} \qquad \text{Equation 1-4}$$

Flueckiger et.al summarize the COP in different kind of heat pumps. For a traditional vapor compression heat pump, the COP can vary from 0.3 to 1.1 if the difference of temperature is 20K. Compared with the thermoelectric cooler, the chemical heat pump system can have a COP of 1.0 to 2.4. [17]

1.1.3 Classification of heat pump

1.1.3.1 Vapor Compression Heat Pump

Vapor Compression Heat Pump is the most widely used in industrial scale. Generally, it uses a specific fluid, hydrofluorocarbon (HFC), as a heat transfer medium. It uses mechanical work such as compressor to provide the required work input.

1.1.3.2 Absorption Heat Pump (Absorption Chiller)

The absorption chiller was first introduced one hundred years ago. The absorption chiller is a kind of refrigerator, it differs from the traditional compression chiller which use traditional mechanical energy. [15] In fact, the cooling effect of absorption chiller is driven by heat source energy. Traditional absorption chiller is either lithium bromide-water (LiBr/H2O) or ammonia-water equipment. The former uses lithium bromide as the absorber and water as the refrigerant, and the latter uses water as the absorber and ammonia as the refrigerant. [16]

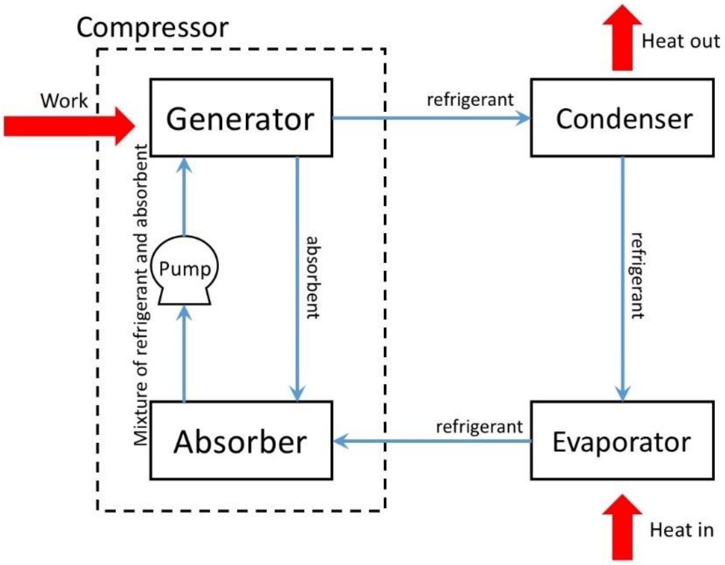


Figure 1-1 Absorption chiller cycle

The major absorption chiller cycle is shown in Figure 1-1. First, refrigerant is evaporated and absorbed by the absorbent in evaporator, this process extracts heat from building or environment. And then the mixture of absorbent and vapor refrigerant goes into the compressor. In absorption chiller, the compressor has absorber, generator and pump. The pump will pump the mixture of absorbent and refrigerant to the generator. In generator, the refrigerant will be extracted and then the refrigerant will go to condenser. Thus, the whole process in compressor drives refrigerant back out of the absorbent and makes those two separated. The refrigerant then goes to the condenser to be cooled back down to a liquid, in the meantime the absorbent is pumped back to the absorber. At last, the liquid refrigerant is released through into the evaporator mentioned above and then the cycle repeats.

The traditional absorption chiller has a lot advantages. Absorption chiller cycle uses very little electricity compared to an electric motor-driven compression cycle chiller. Absorption chiller also allows the use of variable heat resources energy: directly using a gas burner, waste water heat in the form of hot water or low-pressure steam. [17] The absorption chiller can be available in flexible configurations and be used in a variety of fields.

However, the absorption chiller has some problems, such as the size and weight, which will be discussed later.

1.1.3.3 Chemical Heat Pump

Chemical heat pump has attracted some interest in recent years. Chemical heat pump generally uses reversible chemical reactions, and it absorbs or releases energy by breaking or reforming chemical bonds. [11] This part will discuss further below.

1.1.4 Pros and cons of different heat pump

Traditional vapor compression heat pump is relatively inexpensive, it has been widely used in industrial field. [38] However, in recent years, scientific research found that the medium liquid used in vapor compression heat pump, chlorofluorocarbons (CFC) and its replacement hydrofluorocarbons (HFC), can cause an environmental problem. CFC has been discovered that it contributes to the ozone depletion and its replacement HFC is a kind of greenhouse gas and can cause severe greenhouse problem.

Because of these problems, absorption heat pump has attracted considerable interest in past years. Absorption heat pump successfully uses medium which is environmentally friendly. Basically, there are two different types of medium, the first uses lithium bromide as the absorber and water as the refrigerant, and the second uses water as the absorber and ammonia as the refrigerant. Figure 1-2 shows the differences of working between the absorption heat pump and the traditional electric heat pump. From the comparison, we can know that the electric heat pump need electric motor to operate and absorption chiller need the burning of gas or oil to operate. A company name Kawasaki tested absorption chiller using natural gas and the and the conventional electric system using electricity and proved that the absorption chiller can save 51% energy compared with electric heat pump. [44] However, the problems of heat pump are the size, weight, and toxicity. First, absorption heat pump is much larger and heavier than vapor compression heat pump. Because absorption heat pump must use two containers to contain the absorber and refrigerant, and the operation cycle is more complex than the vapor compression heat pump. Second is the toxicity of the media. Both lithium bromide and ammonia are toxic for humans. Furthermore, ammonia will corrode metal for long term use which will shorter the longevity of the heat pump.

Based on these disadvantages, in recent years, a new type of heat pump, chemical heat pump has attracted more and more interest from scientists and researchers because of its simple structure, environmentally friendly medium, high COP and its stability.

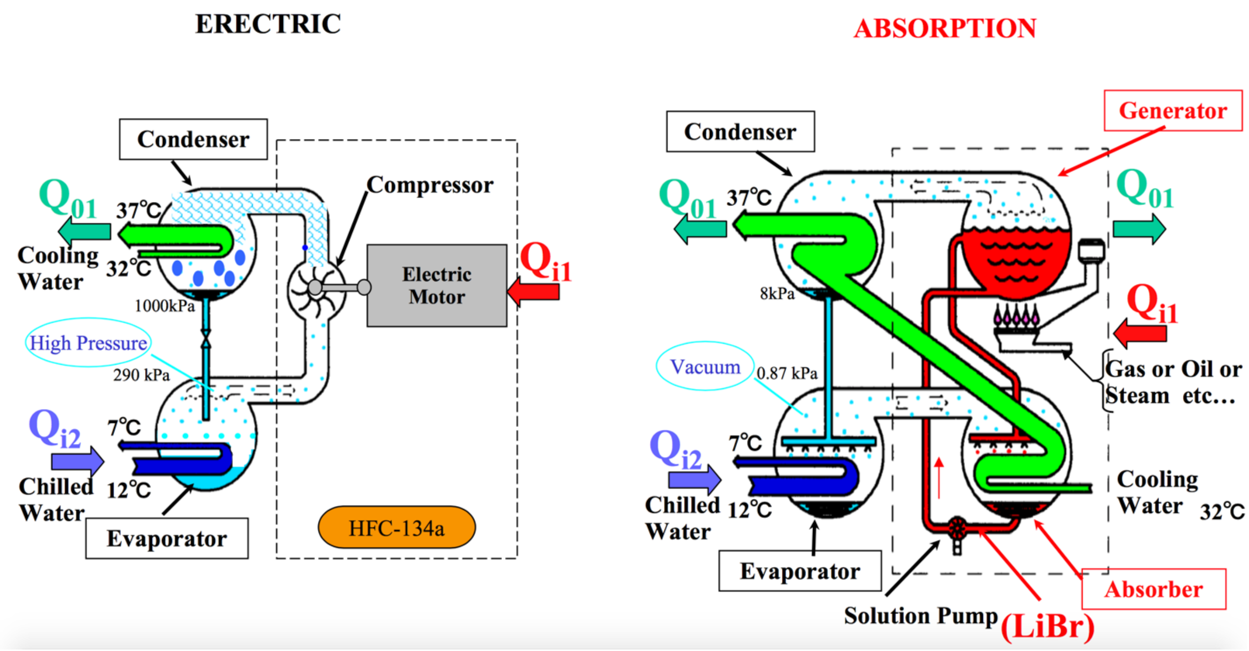


Figure 1-2 “Principle of electric heat pump and absorption heat pump” from Kawasaki

1.2 CHEMICAL HEAT PUMP

In general, a chemical heat pump use a reversible endothermic reaction to replace the liquid-vapor phase change in traditional vapor compression heat pump and absorption heat pump. Because the chemical heat pump can avoid compression and additional system space about the absorption cooling components, the chemical heat pump saves a lot of space and can have the potential to minimize the volume of the whole system.

Based on different kinds of materials of the reactants, the chemical heat pump can mainly be divided into three different categories: chemical heat pump using gas-gas reaction, gas-liquid reaction and gas-solid reaction.

1.2.1 Classification of Chemical Heat Pump (CHP)

1.2.1.1 CHP using gas-gas reaction

The first important gas-gas reaction using in chemical heat pump is dissociation of ammonia. This reaction is used to store thermal energy, especially used in solar energy system. The chemical reaction shows below:

$$2NH_3 + \Delta H \leftrightarrow N_2 + 3H_2$$

In this system, there are two reactors which are energy-store reactor for solar dissociation and energy-release reactor. Both reactors need catalysts. Dunn et al. [19] summarized the ammonia reaction system used in the solar system and described the principle that how the reaction stores the energy for the concentrating solar power.

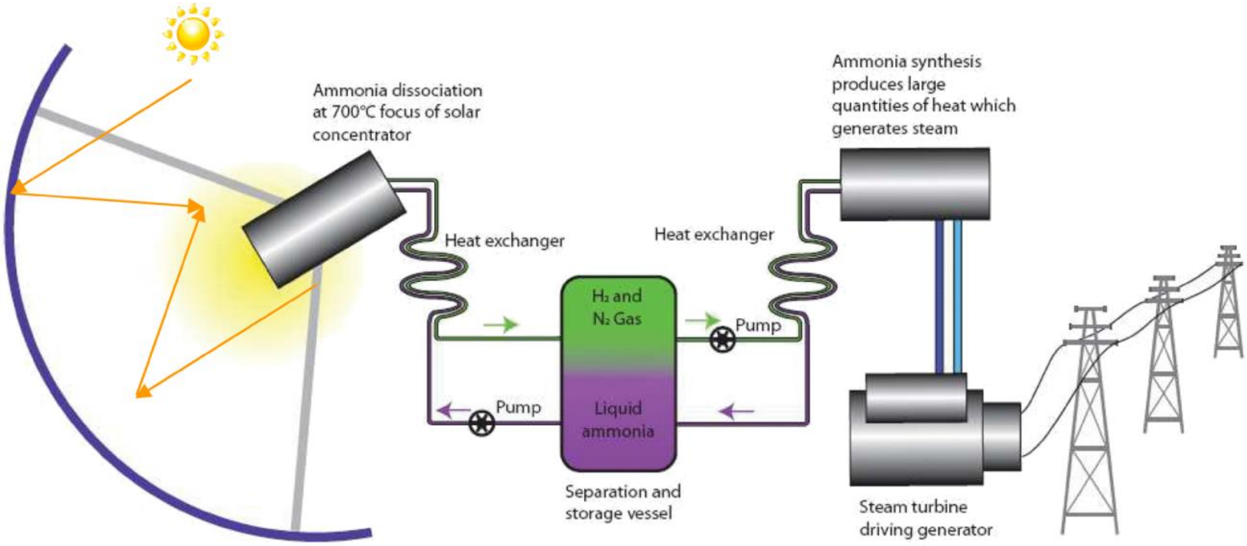


Figure 1-3 Working principle of ammonia reaction heat pump in a solar energy system [19]

The figure 1-3 shows how the ammonia reaction works in the solar energy system. First a mirrored dish focuses solar radiation into a reactor into which ammonia is pumped. And then the catalyst will facilitate the reaction of dissociation at a high temperature into gaseous nitrogen and hydrogen. After dissociation, nitrogen and hydrogen will move into a synthesis reactor. In this reactor ammonia will be regenerated and the whole reaction releases heat and generates stream. The stream will drive the generator to generate electricity.

The advantage of this reaction is that the temperature of this reaction fits the solar concentrators well, and the backward exothermic reaction can proceed easily. However, the endothermic reaction needs a high temperature and the exothermic needs a high pressure (10 – 30 MPa), the long-term stability and cost are the problems.

Another gas-gas reaction used in chemical heat pump is sulfur trioxide (SO_3) dissociation reaction: [20]

$$4SO_3 \leftrightarrow 4SO_2 + 2O_2$$

Similar to ammonia reaction, the dissociation of sulfur trioxide happens at high temperature (1073 – 1273K), which fits well with the solar concentrators. And this dissociation has no undesirable side reactions based on appropriate catalysts, such as vanadium pentoxide [38], Fe-030IT (a finely divided Fe_2O_3 supported on alumina) [40].

The two reactions in the chemical heat pump discussed above are both suited for high temperature. The decomposition of methanol (CH_3OH) happens at relatively low temperature (150 – 200 ℃). Furthermore, methanol is relatively non-toxic and cheap and can be transported and stored conveniently. The basic reaction of this kind of chemical heat pump is:

$$CH_3OH \leftrightarrow 2H_2 + CO$$

In this reaction, the dissociation part is endothermic and the reverse reaction is exothermic. Liu and Yabe proposed a novel two-step reaction method. [21] The whole gas-liquid methanol reactions are shown as follows:

$$CH_3OH + CO = CH_3OOCH$$

$CH_3OOCH + 2H_2 = CH_3OH$

$CO + 2H_2 = CH_3OH$

The advantage of Liu and Yabe's system is that it can minimize the heat loss over a long distance transport. Figure 1-4 shows the schematic diagram of the thermal energy transport system by decomposition and synthesis of methanol in Liu and Yabe's research.

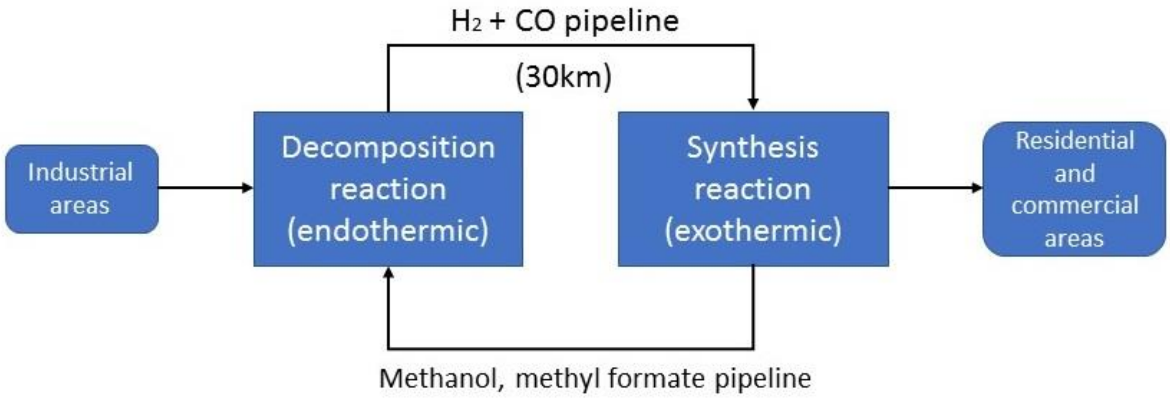


Figure 1-4 Schematic diagram of the thermal energy transport system

Liu and Yabe mentioned for the two-step methanol synthesis reaction which has a 90% conversion ratio, the simulation result proves that the system can gain a 75% heat transport efficiency base. In the meanwhile, for one-step methanol reactions can only gain 52% for heat transport system.

However, even though the operational temperature of methanol is relatively lower than the ammonia reaction and sulfur trioxide reaction, it still has an operational temperature which is higher than 423K. [21] However, for all reactions above, they cannot work well in a lower operating temperature, such as room temperature or 300K – 350K [19]. A lower temperature will cause some challenges because of the reduced rates of reactions with low temperatures. And this pushes scientists to find more kinds of reactions fit for low temperatures.

1.2.1.2 CHP using gas-liquid reaction

In order to work with in the temperature ranges mentioned above, some gas-liquid reactions such as paraldehyde ($C_6H_{12}O_3$) depolymerization and 2-propanol ($(CH_3)_2CHOH$) dehydrogenation have been studied. The basic reaction for paraldehyde depolymerization is:

$$C_6H_{12}O_3 \leftrightarrow 3\,CH_3CHO$$

The structure of paraldehyde is shown in Figure 1-5.

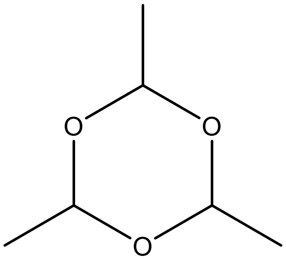


Figure 1-5 Structure of paraldehyde

Paraldehyde reversibly depolymerizes to acetaldehyde when the system is in contact with an acid catalyst, Amberlyst resin. [22] Chong et al. concluded that the conversion of the reaction process can be divided into four steps [23]:

1. the paraldehyde molecule is adsorbed at the catalyst.
2. ring of the molecule opens and produces acetaldehyde.
3. linear chain decomposes.
4. the acetaldehyde desorbed from the catalyst site.

Kawasaki et al. [24] investigated the reaction process based on the experiments and concluded that the rate-determining step is the ring-opening process. Furthermore, catalyst is used in this paraldehyde/acetaldehyde cooling system. The catalyst is an acid resin catalyst and the depolymerization rate is tested in a temperature range from 286K to 303K, based on the experiment result of Kawasaki.

In 1980 Prevost and Bugarel [25] first proposed to use 2-propanol dehydrogenation for a chemical heat pump, the dehydrogenation of 2-propanol reaction has been widely evaluated. The basic reaction is:

$$CH_3CH(OH)CH_3 \leftrightarrow (CH_3)_2CO + H_2$$

At atmospheric pressure, the optimum endothermic reaction temperature occurs at about 350K. At that temperature, the propanol dehydrogenates to acetone and hydrogen. And the optimum temperature of the reverse exothermic reaction occurs at about 470K.

However, based on the discussion of Flueckiger et al., with both chemical reactions, paraldehyde/acetaldehyde system and 2-propanol system, the limit to use them widely is the thermodynamic equilibrium constant, it must be overcome for a sustainable heat pump operation. [17]

1.2.1.3 CHP using gas-solid reaction

In addition, there are some kinds of chemical heat pump using gas-solid reactions, such as CaO, ZnO, PbO, etc reactions [27-30]. The reactions of these kinds of CHP show in the following:

$$CaO + H_2O \leftrightarrow Ca(OH)_2$$

$$Zn + O_2 \leftrightarrow 2ZnO$$

$$PbO + CO_2 \leftrightarrow PbCO_3$$

However, because they are not used widely in chemical heat pump, they will not be discussed further here.

1.3 DISADVANTAGE OF CHP WITH THESE REACTIONS

To summarize the principles of the chemical heat pump, typically one uses a endothermic reaction occurs at low temperature environment:

$\Delta + \mathrm{A} \rightarrow \mathrm{B}$

In this reaction, Δ is the heat that the reaction absorbs from the environment. Then material B is transported to a higher temperature environment where there the exothermic reaction occurs:

$B \rightarrow A + \Delta$

the heat of the reaction is released into the environment. The figure 1-6 shows the principle of the traditional chemical heat pump.

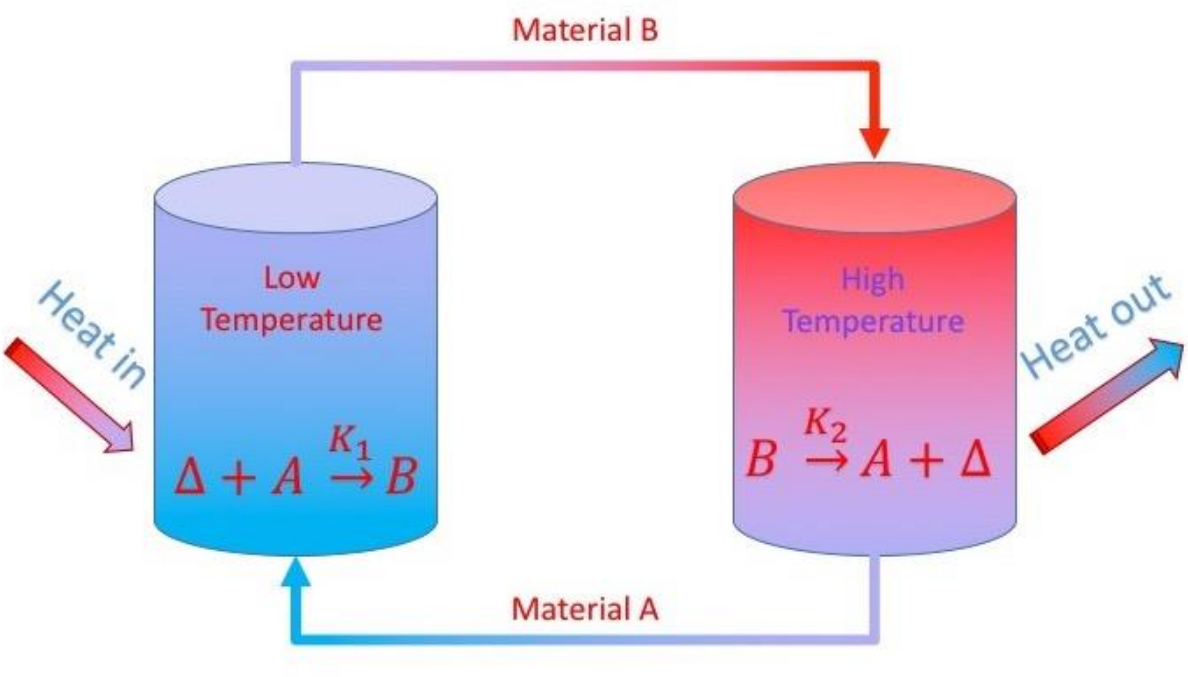


Figure 1-6 Principle of the traditional chemical heat pump

In this system, there will be two reactions:

$$\Delta + \mathrm{A} \rightarrow \mathrm{B} \qquad \mathrm{K}_1$$

$$B \rightarrow A + \Delta \qquad \mathrm{K}_2$$

Here defines $K_1 = [B]/[A]$ and $K_2 = [A]/[B]$. It means $K_1 = 1/K_2$. The first reaction is endothermic and has an equilibrium constant K_1, and the second reaction is exothermic and has an equilibrium constant K_2. Generally speaking, a good chemical heat pump will let $K_1 > K_2$, which means the forward reaction should have a much larger equilibrium constant than the backward reaction. In this way, the reaction will absorb in more heat from low temperature environment when the material A goes to material B, this will give a better cooling effect in the low temperature environment. However, in reality, because the backward reaction is exothermic, the equilibrium constant K_2 is always larger than the equilibrium constant K_1 of the forward reaction which is endothermic. Thus, this contradiction restricts the real use of traditional chemical heat pump.

1.4 WHAT ARE WE LOOKING FOR IN A REACTION?

Because the reactions we discussed above cannot satisfy what we really want, we need to think about and find out a reaction that has the following basic elements. First, based on the restriction and contradiction of traditional chemical heat pump, a new system for the chemical heat pump is designed in figure 1-7.

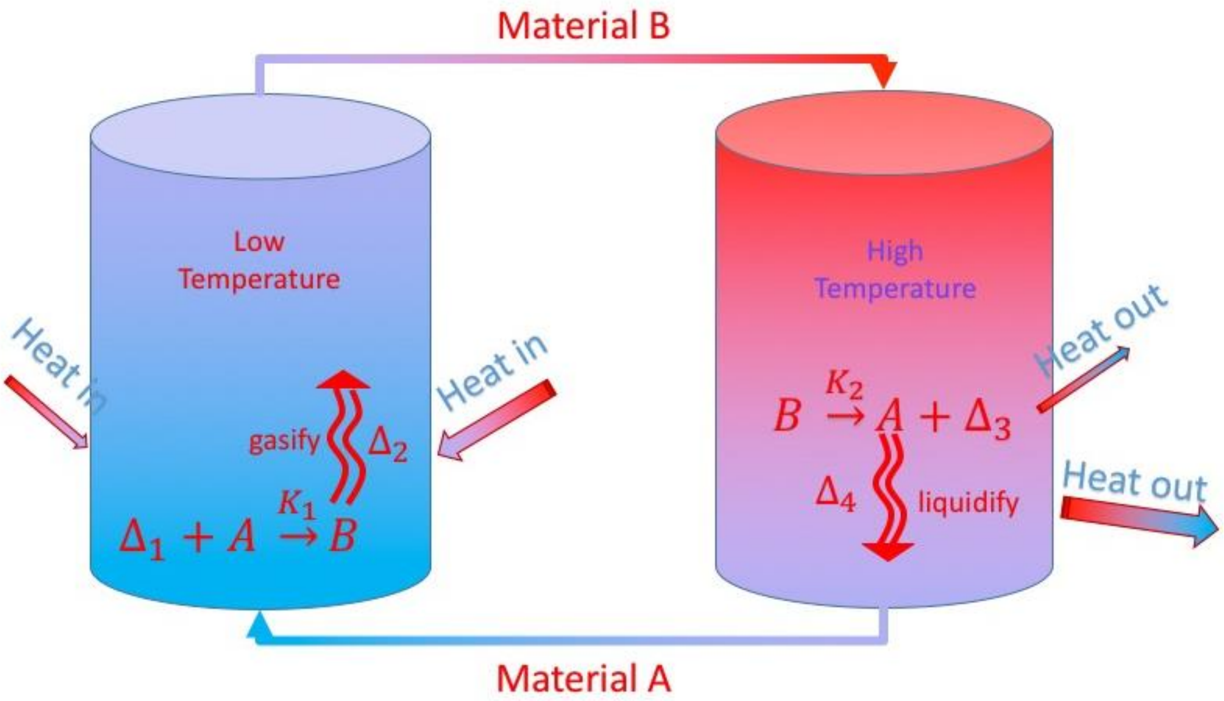


Figure 1-7 Working principle of CHP with new system

In this system, it is a combination of traditional chemical heat pump and traditional heat pump. It means this kind of chemical heat pump combines chemical reaction and phase transfer together. In the lower temperature environment, the endothermic reaction turns material A to B and absorbs in heat from the environment. In this system, the heat of reaction Δ_1 is relatively small, and most of the heat absorbed in depends on the vaporization of material B. To vaporize B will suck in more heat from the low temperature environment. In this way, it will offer a good cooling effect in the low temperature environment. And in the high temperature environment, the exothermic reaction will turn material B to A, and release heat into the high temperature environment. In the meanwhile, phase transformation of A will also release heat. Thus, the heat of reaction Δ_1 and Δ_3 can be relatively small, it means the equilibrium constant will be less temperature dependent and in this way, it is easy to say that the equilibrium constants K_1 and K_2 can satisfy that K_1 almost equals to K_2.

$$\Delta + A \rightarrow B \qquad K_1$$

$$B \rightarrow A + \Delta \qquad K_2$$

Now, how to choose a good reaction in this chemical heat pump should be considered.

1. First of all, the reaction should be reversible. Only reversible reaction can operate the chemical heat pump system with a cycle. And only reversible reaction can satisfy one side of the system is endothermic and the other side is exothermic.

2. The reaction should be predictable. One reason is that a complex reaction might have some unexpected side effects. Thus, there are some possible choices:

a. $A \rightarrow B$

b. $A + B \rightarrow C$

c. $A + B \rightarrow C + D$

3. As mentioned above, the heat of reaction should not be too large. Based on the Van't Hoff Equation:

$$\frac{d\ln K_{eq}}{dT} = \frac{\Delta H^{\ominus}}{RT^2}$$

In this equation, it shows that a reaction with a large heat of reaction $\Delta H^{\ominus}$ will have a significant effect on equilibrium constant, which is not good for using in the chemical heat pump system. If the heat of the reaction is not too large, the equilibrium constant will be less temperature dependent and easier to use in reality.

4. In the new system of the chemical heat pump, gasification is an important way to absorb in heat from the low temperature environment. Thus, it is necessary to make one side of the reaction to be volatile. It means for the equations below:

a. $A \rightarrow B$

b. $A + B \rightarrow C$

c. $A + B \rightarrow C + D$

The left-hand side should be more volatile than the right-hand side.

Based on the considerations discussed above, there are a number of possibilities:

a. Hemiaminal from amine + carbonyl group

Hemiaminal reactions use amine and carbonyl group materials, such as ketone and aldehyde as reactants to produce hemiaminal products. [31] The reaction equation is shown in figure 1-8.

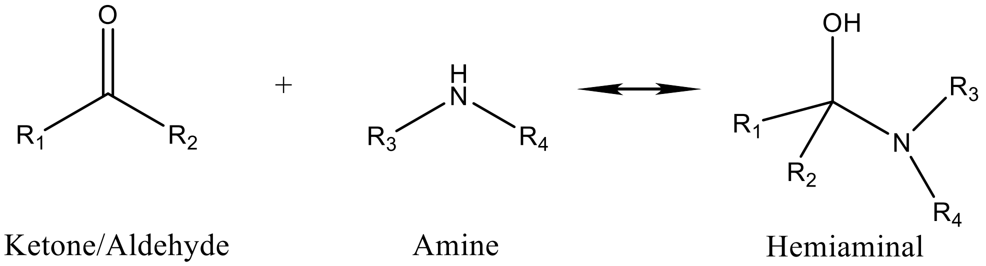


Figure 1-8 Hemiaminal reaction equation

The reason why hemiaminal reactions can be used in the chemical heat pump will be discussed in section 1.5.

b. Olefin Metathesis reaction

Olefin Metathesis reactions use two olefins and scissor and redistribute the fragments of these two olefins and then regenerate new carbon-carbon double bonds [32]. The reaction equation is shown in figure 1-9.

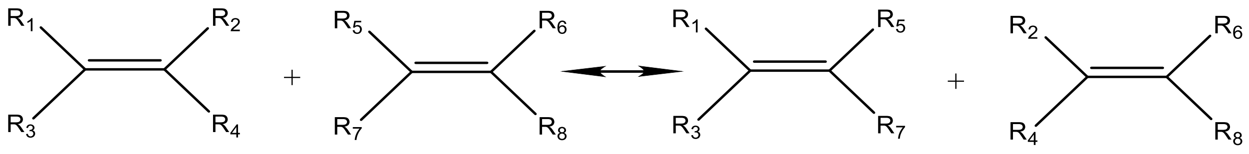


Figure 1-9 Olefin metathesis reaction equation

In the past decades, a lot kinds of efficient catalyst used in the olefin metathesis reactions were invented, such as Ru-based catalysts [41]. Most of the metathesis reactions are reversible because the metathesis process is energetically neutral, [33] it means the reaction can exist both starting materials and the products in a system.

c. Diels-Alder reaction

Diels-Alder reaction is an organic reaction that can transfer a conjugated diene and an olefin into a cyclohexene. [34] The equation of the Diels-Alder reaction is shown in figure 1-10.

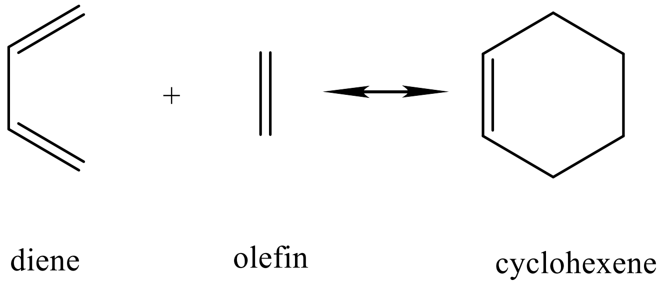


Figure 1-10 Diels-Alder reaction

However, even though it is proved that Diels-Alder reactions can be treated as reversible reactions, this kind of reversible reactions occurs in a high temperature. [35] This feature restricts its application in chemical heat pump.

d. Baylis-Hillman reaction

The baylis-Hillman reaction is a reaction between an activated alkene and an aldehyde. [36] After the reaction, a carbon-carbon bond will generate between the α-position of the alkene and the aldehyde. The equation of the reaction is shown in figure 1-11.

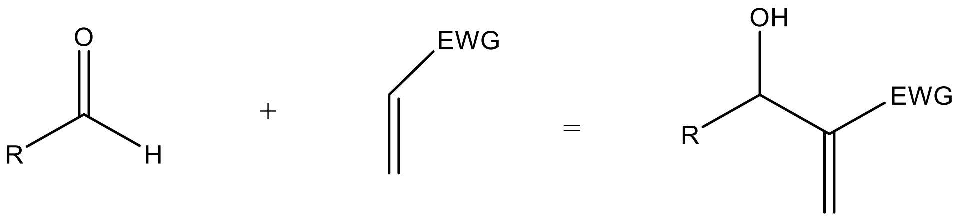


Figure 1-11 Baylis-Hillman reaction

However, Baylis-Hillman reaction has some limitations while using in the chemical heat pump. In most of times, the activated alkene is too active that could cause side reactions. For example, the reaction between an aryl vinyl ketone and an aldehyde, the reactive ketone will first react with another ketone and then add the aldehyde. In this way, there will be some other by-products.

1.5 WHY THE HEMIAMINAL REACTION

In this paper, a chemical heat pump based on hemiaminal reactions is discussed.

The reason why choosing hemiaminal reactions as the reactions used in the chemical heat pump is that hemiaminal reactions typically do not produce by products. Specifically, the equation of hemiaminal reactions can be shown as following:

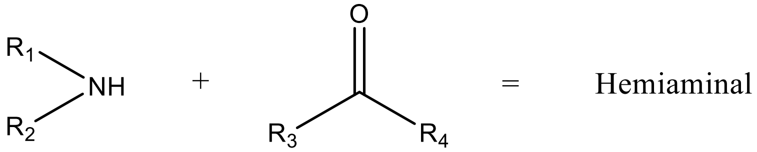


Figure 1-12 General equation of hemiaminal reactions

When the carbonyl group is ketone (R_3 and R_4 are not hydrogen), the hemiaminal reactions will not produce by products. And furthermore, the hemiaminal reaction can be reversible and the boiling point of the product will be bigger than the reactant.

And the most important thing is that there are some available experimental data of the hemiaminal reactions, which can be used to support simulations and to validate the simulation results.

1.6 RESEARCH AIMS

In order to design a new type of chemical heat pump, the following tasks need to be done:

1. Predict equilibrium constant K_{eq} vs. different chemical structures and use the results of equilibrium constant to choose some "candidate hemiaminal reactions".
2. Predict vapor pressure vs. temperature for the "candidate hemiaminal reactions" and narrow the options of hemiaminal reactions.
3. Choose some good "candidate hemiaminal reactions" and do the process design in Aspen Plus and analyze the performance of the chemical heat pump based on the hemiaminal reactions.

2.0 DISCUSSION

The first step is to find some hemiaminal reactions which can satisfy the requirements mentioned above. First, the hemiaminal reactions should be relatively reversible, only reversible reactions can operate the chemical heat pump system with a cycle. And only reversible reaction can satisfy one side of the system is endothermic and the other side is exothermic. To start we assumed we would need reactions with an equilibrium constant between 0.1 to 10. Second, the equilibrium constant of the reaction should not change too much with the change of the temperature. It means the heat of reaction $\Delta H^{\ominus}$ of the hemiaminal reactions should not be too large. Based on the Van't Hoff Equation:

$$\frac{d\ln K_{eq}}{dT} = \frac{\Delta H^{\ominus}}{RT^2} \qquad \text{Equation 2-1}$$

Then we can get the following equation:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{Equation 2-2}$$

It shows that a reaction with a large heat of reaction $\Delta H^{\ominus}$ will have a large effect on equilibrium constant when temperature T changes, which is not good for using in the chemical heat pump system. Because in a chemical heat pump, the reaction occurs in the low temperature, suppose the equilibrium constant is K_1, is endothermic. And the reaction occurs in the high temperature, which the equilibrium constant is K_2, is exothermic. Generally speaking, a good chemical heat pump will let $K_1 > K_2$, which means the reaction in the low temperature should have a larger equilibrium constant than the reaction in the high temperature. In this way, the reaction will absorb in more heat from low temperature environment when the material A goes to material B, this will give a better cooling effect in the low temperature environment. However, if the heat of reactions is large and the reaction in high temperature is exothermic, the equilibrium constant K_2 is always larger than the equilibrium constant K_1 which is endothermic. Thus, this contradiction restricts the real use of traditional chemical heat pump. Based on these requirements, we need to computational calculation to get the equilibrium constant K_{eq} of some hemiaminal reactions and then choose the best one.

The equilibrium constant has a relationship with structures of the materials:

$$\mathrm{K} = \mathcal{F}\ (\mathrm{structure})$$

It means the equilibrium constant can be changed by changing the structures of the reactants of the reaction. Thus, various ways to calculate equilibrium constant by screening different structures with computational simulation are discussed in this paper.

2.1 DENSITY FUNCTIONAL THEORY (DFT)

2.1.1 Fundamentals of DFT

Density functional theory (DFT) is a new type of electronic structure computational calculation and DFT has gained a great popularity in the past several decades [48]. The main goal for DFT is to solve the many body problems. Many body problem in quantum mechanics provide a detailed and accurate description of a molecule. Solving many body problem can help us to analyze some properties of the molecule, such as thermodynamic properties [49].

To solve the many body electron problems, the first step is to solve the Schrodinger equation in order to find the ground state for a collection of atoms:

$$\hat{\boldsymbol{H}}\boldsymbol{\psi}(\{\boldsymbol{r}_i,\},\{\boldsymbol{R}_I\}) = \boldsymbol{E}\boldsymbol{\psi}(\{\boldsymbol{r}_i,\},\{\boldsymbol{R}_I\}) \qquad \text{Equation 2-3}$$

And because of the Born Oppenheimer approximation, the mass weight of nuclei is much larger than the electrons:

$m_{nuclei} \gg m_e$

Thus, the dynamics of atomic nuclei and electrons can be separated, that is:

$$\boldsymbol{\psi}(\{\boldsymbol{r}_i,\},\{\boldsymbol{R}_I\}) = \boldsymbol{\psi}_N(\{\boldsymbol{R}_I\}) * \boldsymbol{\psi}_e(\{\boldsymbol{r}_i\}) \qquad \text{Equation 2-4}$$

And the Schrodinger equation for electrons can be written in the following way:

$$\hat{\boldsymbol{H}}\boldsymbol{\psi}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\dots,\boldsymbol{r}_n) = \boldsymbol{E}\boldsymbol{\psi}(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,\dots,\boldsymbol{r}_n) \qquad \text{Equation 2-5}$$

Here the electronic Hamiltonian consists of three different parts:

$$\hat{\boldsymbol{H}} = -\frac{\bar{h}^2}{2m_e}\sum_i^{N_e}\nabla_i{}^2 + \sum_i^{N_e}\boldsymbol{V}_{ext}(\boldsymbol{r}_i) + \sum_{i=1}^{N_e}\sum_{j>1}\boldsymbol{U}(\boldsymbol{r}_i,\boldsymbol{r}_j) \qquad \text{Equation 2-6}$$

The first part of the right-hand side is the potential energy of electrons, and the second part is the force between nuclei and electrons, the third part is the force between the electrons. And the heart part of DFT is Hohenberg and Kohn theorem. The theorem one of Hohenberg and Kohn theorem is the ground state energy E is a unique functional of the electron density [50]:

$$\mathbf{E} = \mathbf{E}[\mathbf{n}(\mathbf{r})] \qquad \text{Equation 2-7}$$

The theorem two of Hohenberg and Kohn theorem is that the electron density that minimizes the energy of the overall functional is the true ground state electron density:

$$\mathbf{E}[\mathbf{n}(\mathbf{r})] > \boldsymbol{E}_0[\boldsymbol{n}_0(\boldsymbol{r})] \qquad \text{Equation 2-8}$$

Thus, the energy functional can be written:

$$\mathbf{E}[\{\psi_i\}] = E_{known}[\{\psi_i\}] + E_{XC}[\{\psi_i\}] \quad \text{Equation 2-9}$$

$$E_{known}[\{\psi_i\}] =$$

$$-\frac{\hbar}{m_e}\sum_i \int \psi_i^* \nabla^2 \psi_i d^3r + \int V(r)n(r)d^3r + \frac{e^2}{2}\iint \frac{n(r)n(r')}{r-r'} d^3r d^3r' + E_{ion} \quad \text{Equation 2-10}$$

Here, the right-hand side are electrons potential, force between electrons and nuclei, force between electrons, and force between nuclei.

And $E_{XC}[\{\psi_i\}]$ is exchange-correlation functional, which includes all quantum mechanical terms and some approximation. Some simplest and famous XC-functional approximations are local density approximation (LDA) and generalized gradient approximation (GGA). LDA approximates the true density energy by a local constant density [51]. An improvement to the LDA is GGA [52]. GGA considers the gradient of the electron density. GGA can be written as:

$$E_{xc} = E_{xc}[\rho(r), \nabla\rho(r)] \quad \text{Equation 2-11}$$

It has to be mentioned another important scheme is the Kohn-Sham scheme. The scheme is a modification of Hohenberg-Kohn scheme. Kohn and Sham rewrite the Hohenberg-Kohn scheme by approaching to the interacting electrons problems [43]. Both Hohenberg-Kohn scheme and Kohn-Sham scheme built the heart part of the DFT.

In physic and chemistry field, DFT plays an important role because scientists can use DFT to predict a great variety of different molecule properties, such as molecule structures, vibrational frequencies, atomization energy and some other important thermodynamic properties, including heat of formation, Gibbs free energy, etc.

There are many DFT methods, such as B3LYP, TPSSh, PBE, M06-2X, etc [53]. Different method can solve specific problems. Different methods are based on different approximation. For example, B3LYP, TPSS and PBE are based on GGA calculations. They have a good performance when calculating transition metal compounds. And for organic and main group molecules, M06-2X is a better choice which is based on hybrid GGA approximation.

In this paper, the DFT is proposed to estimate some thermodynamic properties such as heat of formation and Gibbs free energy. the results of the heat of formation can be calculated to get the heat of reaction of the hemiamial reaction. That is:

$$\text{reactant 1} + \text{reactant 2} \Rightarrow \text{hemiaminal}$$

$$\Delta H_{reaction} = \Delta H_{formation\_hemiaminal} - \Delta H_{formation\_reactant1} - \Delta H_{formation\_reactant2}$$

And in the same way, the Gibbs free energy of reaction can be calculated:

$$\Delta G_{reaction} = \Delta G_{formation\_hemiaminal} - \Delta G_{formation\_reactant1} - \Delta G_{formation\_reactant2}$$

Under standard conditions, the Van’t Hoff equation can be introduced:

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H}{RT^2} \qquad \text{Equation 2-12}$$

Where, K_{eq} is the equilibrium constant of the reaction, R is the ideal gas constant and ΔH is the reaction enthalpy, or it can be said heat of reaction. And the Van’t Hoff equation can be derived as:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{Equation 2-13}$$

Thus, the change of the equilibrium constant can be calculated if the heat of reaction can be known. Plus, it is known that:

$$\Delta G^{\circ} = -\mathrm{RT}\ln K_{eq} \qquad \text{Equation 2-14}$$

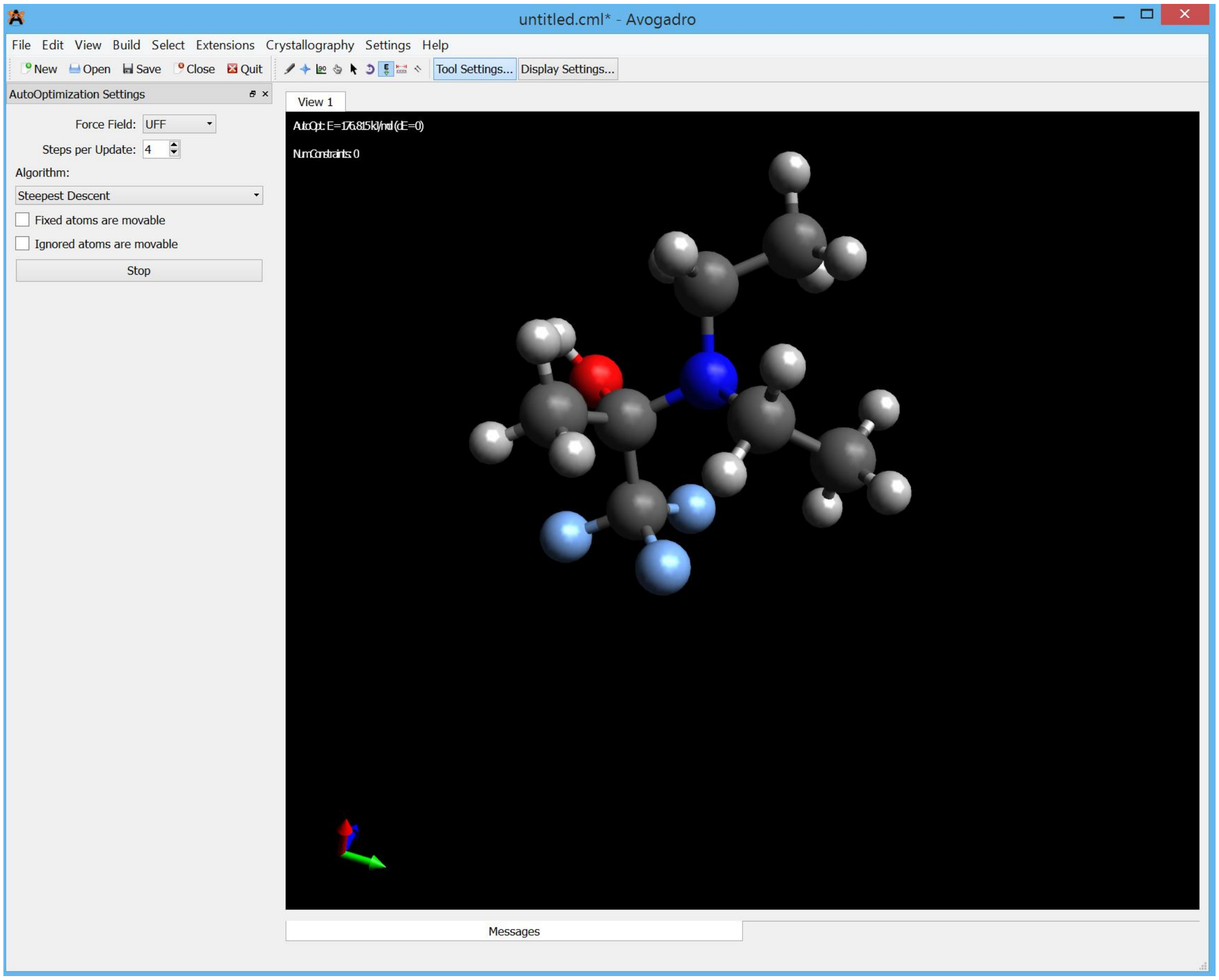
The equilibrium constant in standard condition can be calculated if the Gibbs free energy of the reaction can be known. And that’s why DFT is used to calculate the heat of reaction and Gibbs free energy of reaction for hemiaminal reactions.

2.1.2 Doing DFT calculations

The software used to calculate thermodynamic properties are Avogadro and Gaussian 09. Avogadro allows user to draw structure of a molecule and make a simple optimization locally and generate an extension file and then put the extension file in Gaussian 09 and Gaussian 09 can use the data to optimize and calculate the thermodynamic data.

Here is the procedure that how to make a computational simulation based on DFT method and then get the thermodynamic properties of a specific molecule. The procedure use hemiaminal product of reaction between 1,1,1-Trifluoroacetone and diethylamine as an example.

Draw structure of the molecule in Avogadro and do a simple auto optimization first. The reason why doing this optimization is to shorten and save some time when doing the optimization in the future. In Avogadro optimization page, choose UFF as a force field and choose steps per update as 4. Optimization of these two parameters can satisfy both time saving and accuracy. The auto optimization tool page shows in figure 2-1.



Force Field: UFF
Steps per Update: 4
Algorithm:
Steepest Descent
☐ Fixed atoms are movable
☐ Ignored atoms are movable

```
AutoOpt: E=176.815 kJ/mol (dE=0)

NumConstraints: 0
```

Figure 2-1 Auto optimization tool page in Avogadro

When finish optimization, go to extensions list and choose Gaussian as the output file. It is an .com output file and can be opened by the Gaussian 09 software in the local computer. The file contains the DFT method chosen, for example, B3LYP, and the basis, for example, 6-311G*, as well as the relative locations of all different atoms. And it can be added some other requirements, for example, ‘opt’ is for optimization of this molecule and ‘fre’ is for calculation of the molecule’s vibration frequency.

Based on the calculation restriction of local computer or laptop, Simulation and Modeling (SAM) is used to do the calculation. SAM can be treated as the super computer of University of

Pittsburgh, and it is a center for university students and faculties to advance the application of computing to do research.

After all preparation, change the file after optimization by local computer to a .gzmat file, because Frank cannot recognize .com file. For help and detail, the helper page of Frank can be visited. (http://core.sam.pitt.edu/frank)

In order to submit request, it is needed to create a submission file, just like follow:

```
#!/bin/bash
#PBS -N g09
#PBS -j oe
#PBS -l nodes = 1 : ppn = 1
#PBS -q shared
#PBS -l walltime = 1:00:00
cd $PBS_O_WORKDIR
module load Gaussian/g09B.01
g09 < hemiaminal.gzmat > hemiaminal.g09
```

the script means that you must run in node = 1 and ppn = x, where x is the memory the user required and the longest run time is 1 hour in this script. The last line in this script is that to use the all information in hemiaminal.gzmat file and after calculation will generate a file named hemiaminal.g09.

Now the user can write code in putty’s command line just like “qsub submission” if the script file above named subsmission. Remember to calculate optimization first and then do the calculation of frequency in Frank, in order to make sure the result is accurate.

After calculating frequency, there will be a .g09 file in the user's space in Frank. The result data which are useful show as follows:

Zero-point correction= 0.102763 (Hartree/Particle)

Thermal correction to Energy= 0.108716

Thermal correction to Enthalpy= 0.109660

Thermal correction to Gibbs Free Energy= 0.074612

Sum of electronic and zero-point Energies= -211.182770

Sum of electronic and thermal Energies= -211.176817

Sum of electronic and thermal Enthalpies= -211.175872

Sum of electronic and thermal Free Energies -211.210920

the unit above is Hartree. The conversion factor is that 1 Hartree = 627.5095 kcal/mol. Now with the sum of electronic and thermal enthalpies and sum of electronic and thermal free energies, the reaction enthalpies and the Gibbs free energy of reactions can be calculated.

2.1.3 Results and discussions

Now is to do a screening of different structures to find some reactions with "good" result. Here, "good" means the reaction is reversible, has an equilibrium constant between 0.1 and 10, and also means the reactants should be volatile. First is to analyze the mechanism of the hemiaminal reactions.

Figure 2-2 is the general equation of the hemiaminal reaction:

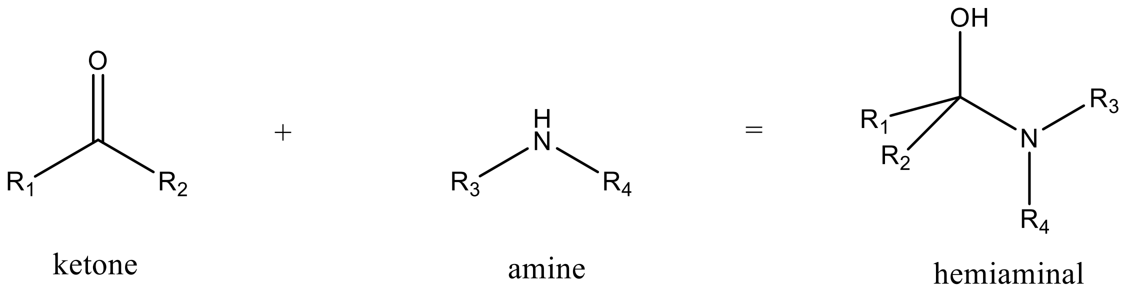


Figure 2-2 Hemiaminal reaction

In this reaction, amine is deployed as nucleophiles and react with an electron-deficient carbonyl group. Here, the driving force for the reaction is the formation of a nucleophile functional group N^-, in the meanwhile carbonyl group is an electron-poor functional group. Thus, it can be concluded that a ketone with R1 and R2 are electronic withdrawing and an amine with R3 and R4 are electronic donating will promote occurrence of the reactions. Table 2-2 shows different electronic donating or electronic withdrawing group. Here “Level” means the strength of the electron donating effect or election withdrawing effect. Level 1 means it has a strongly electron donating effect and Level 5 means it has a strongly electron withdrawing effect.

Table 2-1 Summary of electronic donating and withdrawing group

Level 1 (electron strongly donating)	Level 4
$-O^-$	-CHO
$-NR_2$	-COR
-NHR	-COOH
$-NH_2$	-COCl
-OR	-COOR
-OH	$-CONH_2$
Level 2	Level 5 (electron strongly withdrawing)
-NHCOR	$-CF_3$, $-CCl_3$
-OCOR	-CN
Level 3	$-SO_3H$
-R	$-NH_3^+$
$-C_6H_5$	$-NR_3^+$
$-CH=CR_2$	$-NO_2$

Based on table 2-2, some reactions can be simulated and calculated as a test, as shown in table 2-3.

Table 2-2 Some test results based on DFT calculation

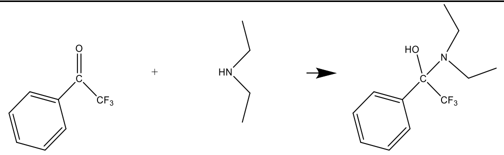
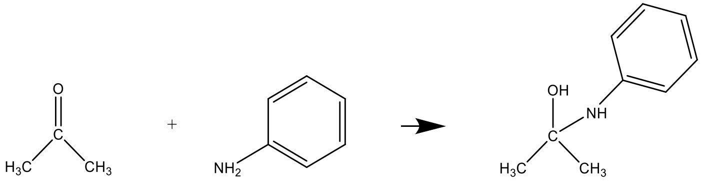
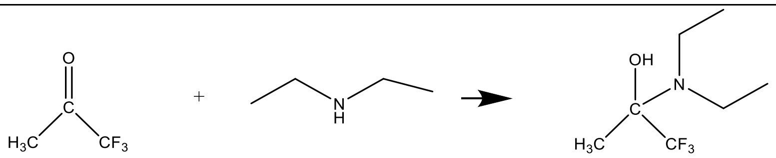
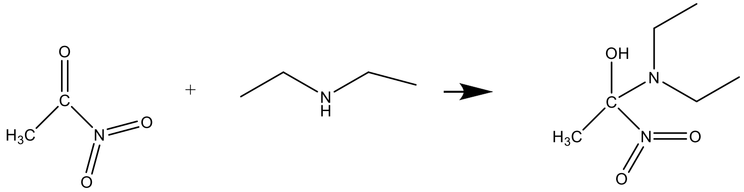
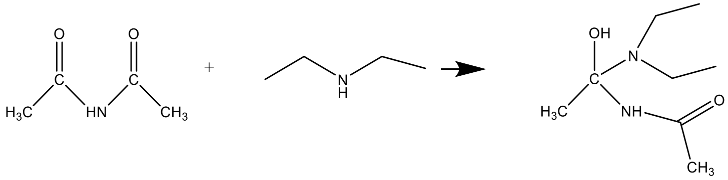
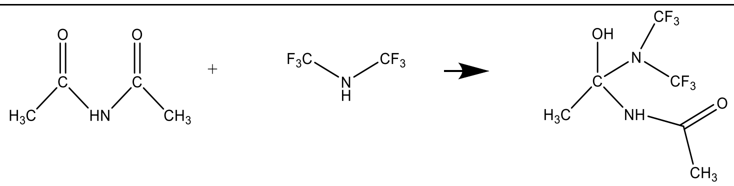
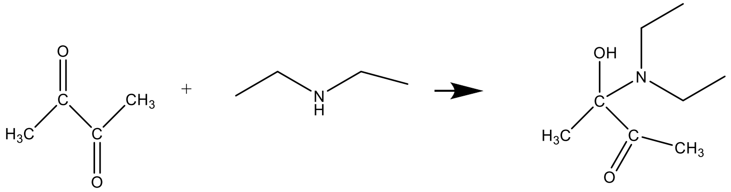
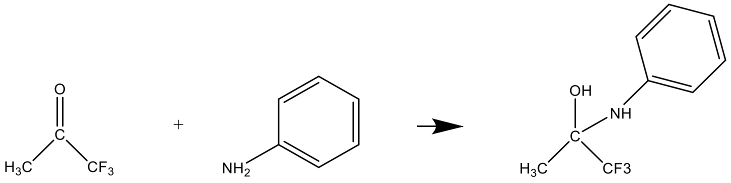
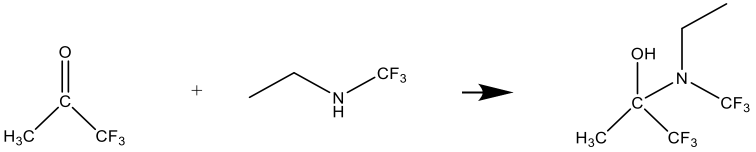
Number	Reaction	K_{eq}
1		0.07
2		$1.4*10^{-5}$
3		540
4		99
5		$8.0*10^{-5}$
6		$2.69*10^{-11}$

Table 2-2 (continued)

7		$3.38*10^{-3}$
8		4.1
9		$2.7*10^{-5}$

Compared reaction 1 and reaction 3. The ketone in reaction 1 has two electronic withdrawing groups: phenyl and trifluoromethyl, but equilibrium constant of reaction 1 is much lower than reaction 3. The reason is that phenyl has a steric hindrance, it prevents amine to attack carbonyl group.

When adding an electronic withdrawing group on amine, it will decrease the equilibrium constant. The results support this opinion. (compare reaction 5 with reaction 6) On the contrary, we add an electronic withdrawing group on ketone, it will increase the equilibrium constant. (compare reaction 3 with reaction 4 and 5). However, the equilibrium constants of all first 6 reactions are not in the range of 0.1 ~ 10.

Thus, based on reaction 3, change acetone with a weaker electronic group: -COCH3. Its electronic withdrawing effect is weaker than trifluoromethyl but stronger than phenyl. And the result is 3.38 * 10^-3 (reaction 7). And remain trifluomethyl ketone unchanged and add an electronic withdrawing group phenyl to amine, in order to decrease the K of reaction 3. the result is 4.06 (reaction 8), much better now.

The comparison between different reactions shows a consistency with the mechanism of hemiaminal reactions. The next step is to narrow the scope of the reactions and find some reversible ones and in the meanwhile, make a correlation between the simulation results and the experimental results.

In order to narrow the scope of the reactions, the structure of reactants should be changed slightly. That is to only change the structure of ketone or amine at one time and compare the change of equilibrium constant.

Table 2-3 Equilibrium constant results based on DFT calculation

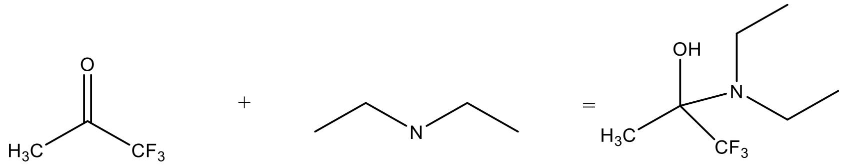
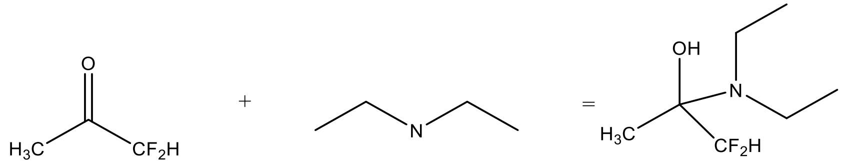
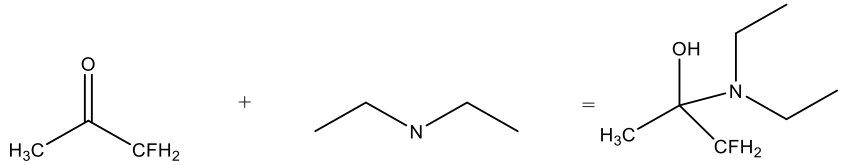
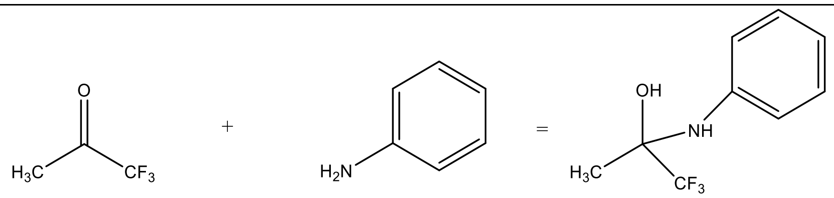
No.	Reaction	K_{eq}
1		540
2		0.01
3		0.002
4		4.1

Table 2-3 (continued)

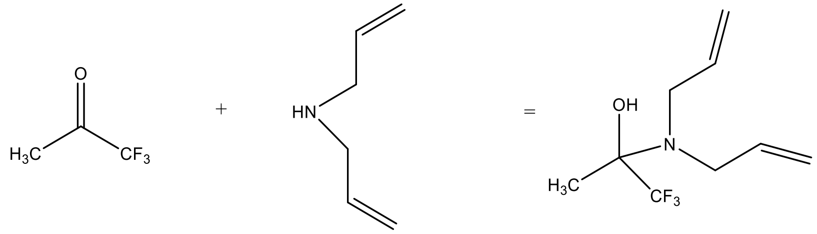
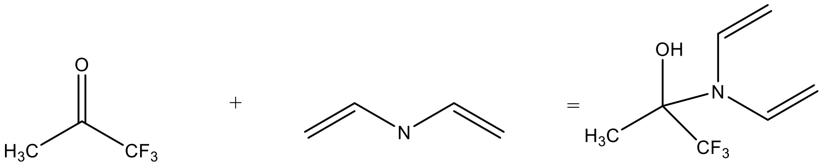
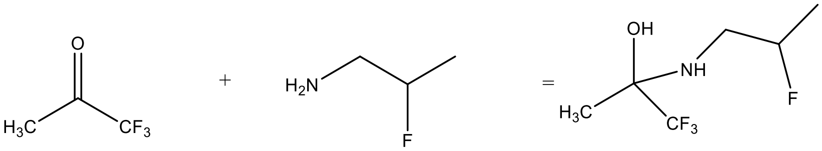
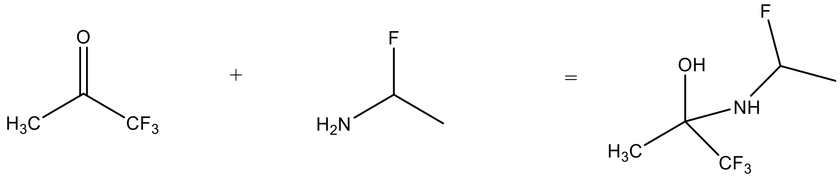
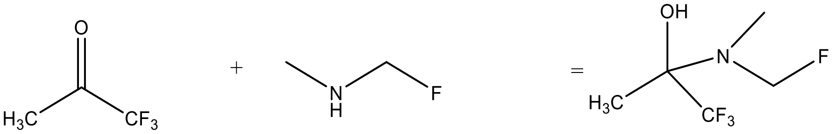
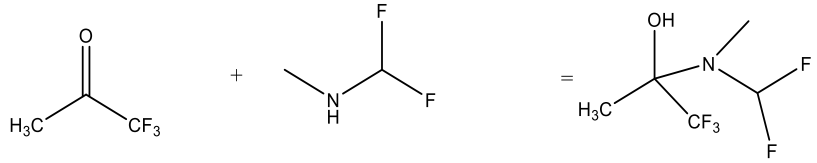
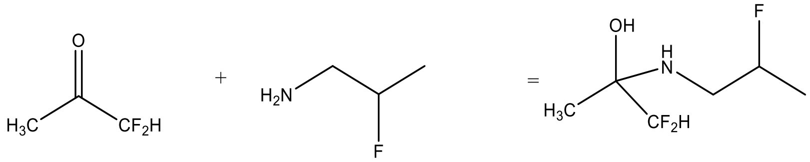
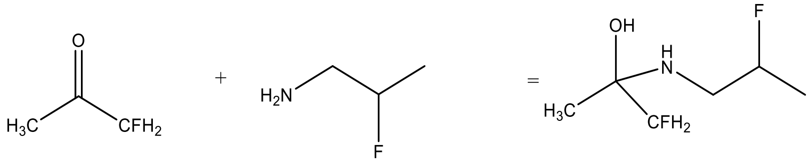
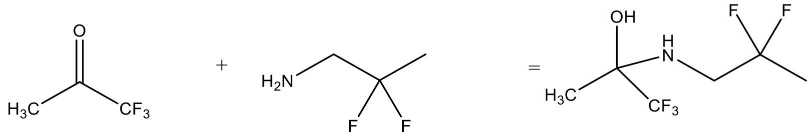
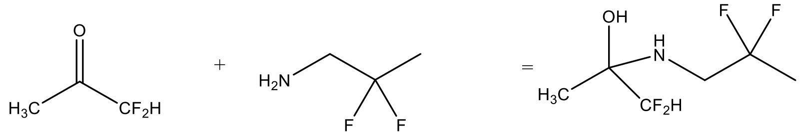
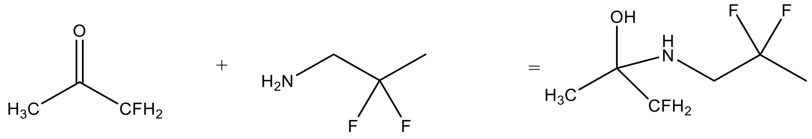
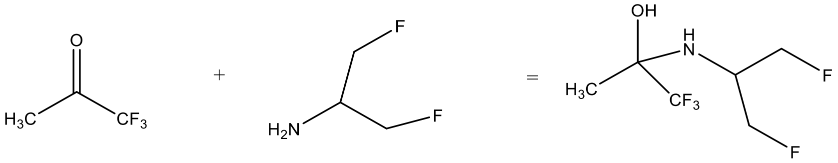
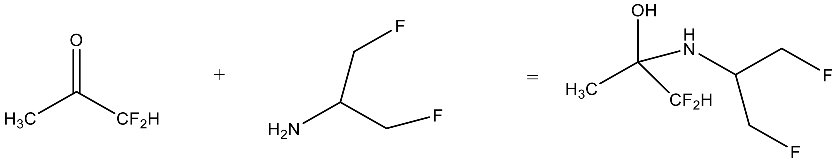
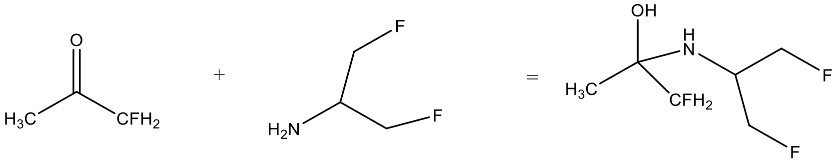
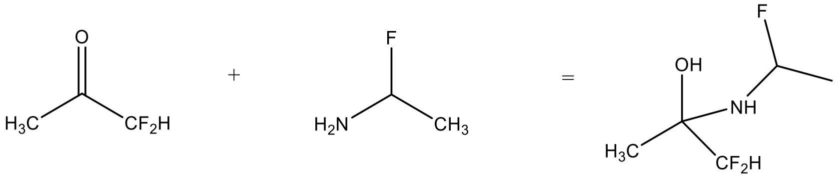
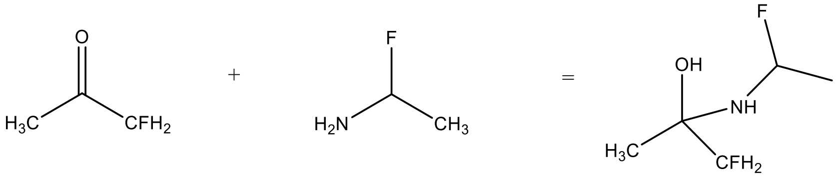
5		28.2
6		4.0*10^{-6}
7		2000
8		6800
9		1.0*10^{4}
10		0.004
11		2.5
12		0.2

Table 2-3 (continued)

13		$1.3*10^4$
14		2.1
15		0.2
16		6.3
17		0.005
18		$4*10^{-4}$
19		$2.6*10^{-4}$
20		0.004

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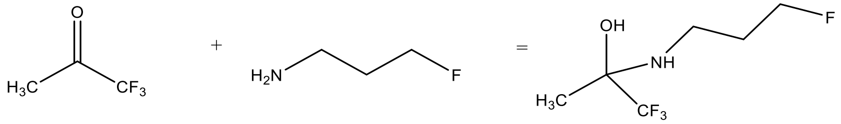
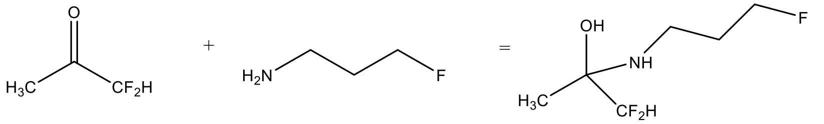
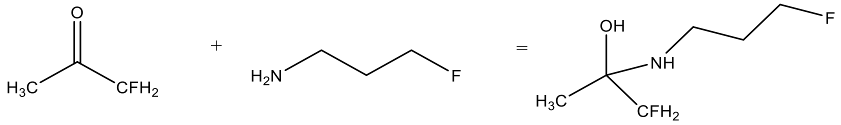
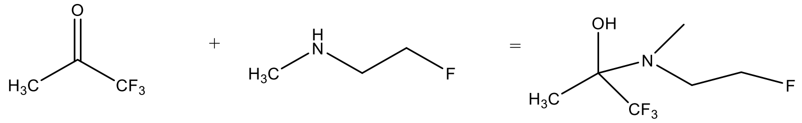
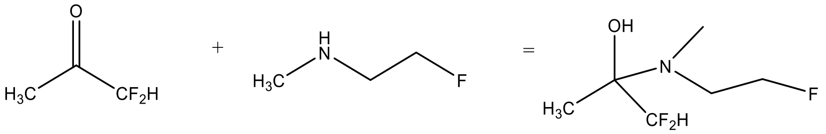
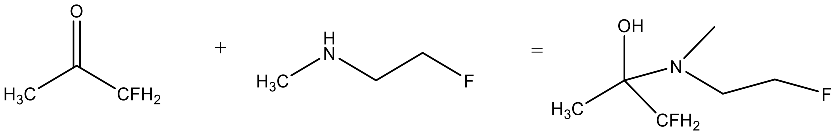
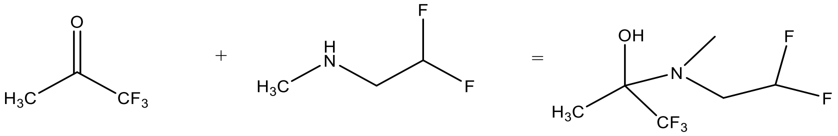
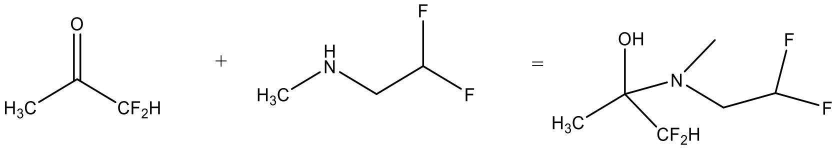
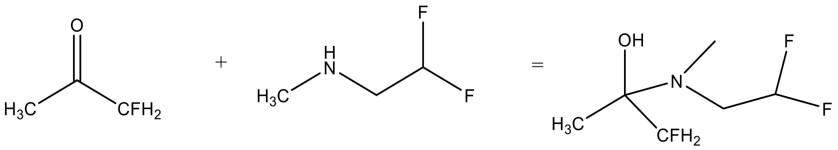
21		12.3
22		1.8
23		0.03
24		0.2
25		0.002
26		0.007
27		0.42
28		0.04
29		0.001

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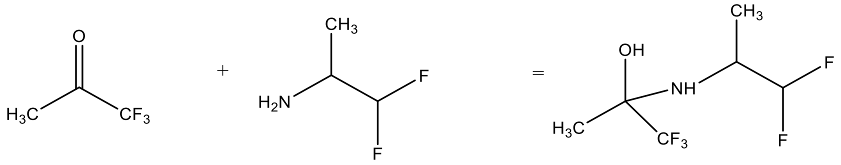
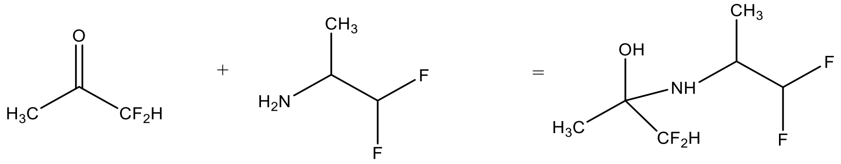
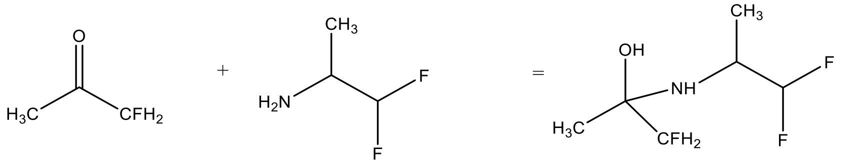
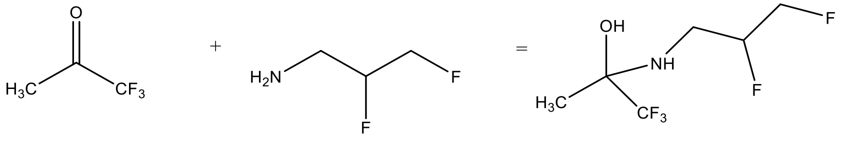
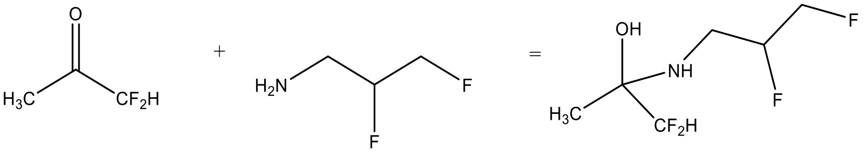
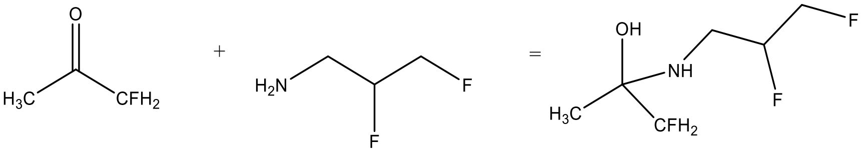
30		0.078
31		0.05
32		0.001
33		248
34		5.4
35		2.4

There are two major ways to change the structure of the molecule. First is that only change the structure of ketone in hemiaminal reaction. It has been discussed above that trifluoromethyl is a strong electronic withdrawing group, and it is a good idea that to change the number of fluorine atom in order to change the effect of the electronic withdrawing, and finally to change the equilibrium constant. Thus, compared with reactions 1, 2 and 3, the structures of ketone changed from 1,1,1-trifluoroacetone to 1,1-difluoroacetone and 1-fluoroacetone. And the results show that the equilibrium constant (K_{eq}) change from 540 with ketone structure 1,1,1-trifluoroacetone to 0.01 with ketone structure 1,1-difluoroacetone and 0.002 with ketone structure 1-fluoroacetone. Thus, when remain amine unchanged and only change structure of ketone, and only change functional group of ketones from a strong electronic withdrawing to weak electronic withdrawing, the equilibrium constant will become lower. In the meanwhile, the similar results can be found among reaction 7, 11, 12; reaction 13, 14, 15; reaction 16, 17, 18; reaction 8, 19, 20; reaction 21, 22, 23; reaction 24, 25, 26; reaction 27, 28, 29; reaction 30, 31, 32; reaction 33, 34, 35.

On the other hand, it also can remain ketone not changed and only change the structure of amine. For example, compare with reaction 1, 4 and 5, the structure of amine changes from diethylamine to aniline in reaction 4, diallylamine in reaction 5 separately. The equilibrium constant of reaction 4 is 4.1, much lower than equilibrium constant in reaction 1. The reason is that phenyl in aniline has a stronger electronic withdrawing effect than ethyl in diethylamine. And in the meanwhile phenyl is larger than ethyl, and it has a stronger steric effect than ethyl.

To summarize, use DFT to calculate some thermodynamic properties, such as heat of formation and Gibbs free energy of different molecules and then use the thermodynamic property data to calculate heat of reaction and Gibbs free energy of different hemiaminal reactions. The equilibrium constant can be calculated by the result of Gibbs free energy of reaction and the change of equilibrium constant of a reaction can also be calculated by known of heat of reaction and Gibbs free energy of reaction. Furthermore, change the structures of amine or ketone separately. It has been proved that with their change of electronic effect, the equilibrium constant can be changed by changing structures of the reactants.

In the meantime, another part need to be done is that to find some experimental equilibrium data and make a comparison between the simulation results and the experimental ones. G.J. Mohr used chromo- and fluororeactands as indicator dyes in a sensor. [45,46] He did different kinds of experiments and one of them is hemiaminal formation with ketone as chemically reactive group and amine as the analyte. There are two different fluororeactands G.J. Mohr used, CR-546 and ETH-4001.

ETH-4001 CR-546

Figure 2-3 Structure of ETH-4001 and CR-546

In order to make a connection between experimental and simulation results, DFT method is also used to calculate Gibbs free energy and then use Gibbs free energy to calculate the equilibrium constant.

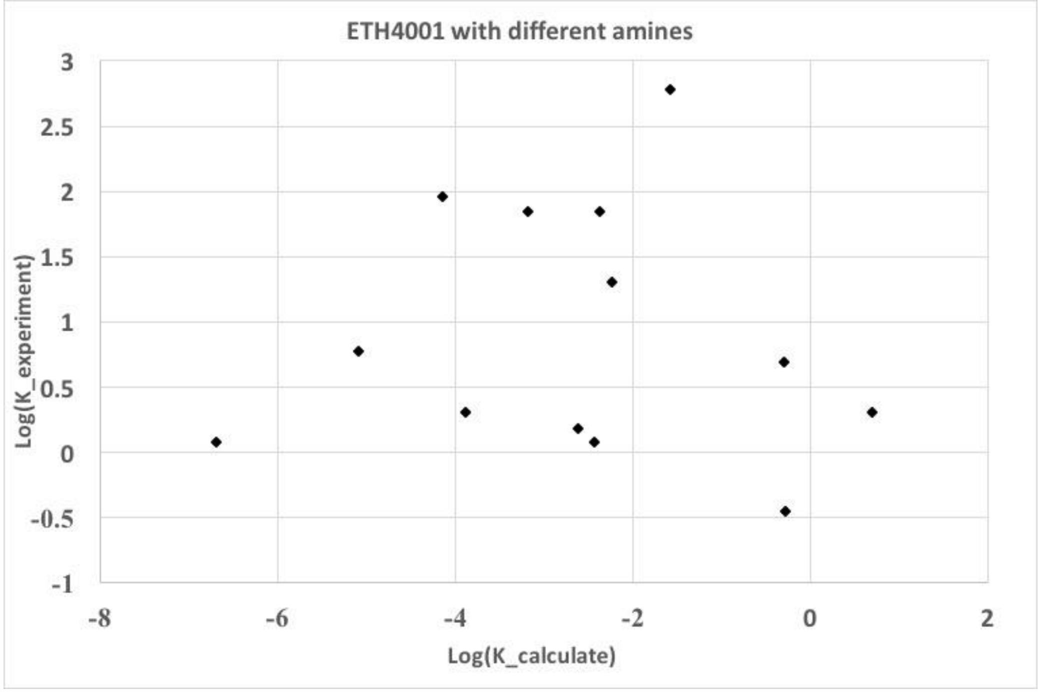
Table 2-4 Comparison of K_{eq} between calculation by this thesis and experiment by literatures

Ketone	Amine	$K_{calculation}$	$K_{experiment}$
ETH-4001	Ammonia	0.52	0.35
ETH-4001	Methylamine	4.96	2
ETH-4001	Ethylamine	0.50	4.9
ETH-4001	Triethylamine	$8.0*10^{-6}$	6
ETH-4001	Propylmaine	$5.8*10^{-3}$	20
ETH-4001	2-propylamine	$3.6*10^{-3}$	1.2

Table 2-4 (continued)

ETH-4001	1-butylamine	$6.6*10^{-4}$	70
ETH-4001	Tert-butylamine	$2.0*10^{-7}$	1.2
ETH-4001	1-hexylamine	0.025	600
ETH-4001	Pyridine	$2.4*10^{-3}$	1.5
ETH-4001	Aniline	$1.3*10^{-4}$	2
ETH-4001	Amphetamine	$4.1*10^{-3}$	70
ETH-4001	Methamphetamine	$7.0*10^{-5}$	90
CR-546	Methylamine	2.08	20
CR-546	Ethylamine	14.72	55
CR-546	Diethylamine	0.13	22
CR-546	Triethylamine	$8.2*10^{-5}$	80
CR-546	Propylamine	0.21	170
CR-546	Butylamine	0.36	750
CR-546	Hexylamine	0.01	6500

Table 2-4 shows the comparison between experimental data and simulation results. From the data in the list, it can be found that span of the simulation results is too large and not consistent with experimental data. In order to show comparison more directly, graphs of comparison of experimental equilibrium constant and calculation equilibrium constant when choosing ETH-4001 and CR-546 as ketone were shown separately (shown in Figure 2-4), and all data will change into natural logarithm value.



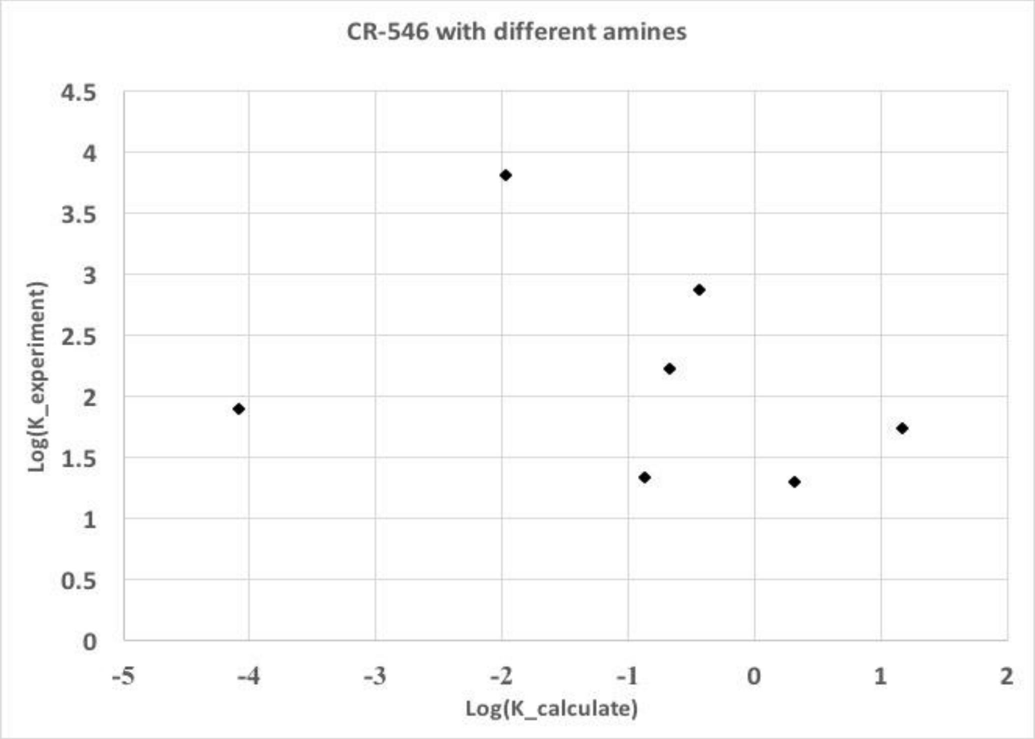


Figure 2-4 $K_{experiment}$ vs $K_{calculation}$ of ETH-4001 and CR-546

It is clear that the data in each graph cannot generate a single fitted curve, even though the data has changed from original one to natural logarithm value. In order to test and prove whether a connection or correlation can be built between experimental equilibrium constant and simulation equilibrium constant value, more experimental equilibrium constant values were found and tested. Sander and Jencks discussed the equilibria about the additions to carbonyl group and some data about hemiaminal formation can be used to compare with simulation results. Sander and Jencks used pyridine-4-carboxaldehyde, formaldehyde and p-chlorobenzaldehyde as the carbonyl group molecules separately to react with different amines.

Table 2-5 shows the experimental equilibrium constant value and simulated equilibrium constant value.

Table 2-5 Experimental and calculation equilibrium constant of selected components

Carbonyl group	Amine	$\text{Log}(K_{\text{experiment}})$	$\text{Log}(K_{\text{simulation}})$
pyridine-4-carboxaldehyde	Methylmaine	1.94	-2.34
pyridine-4-carboxaldehyde	Ethylamine	1.63	-3.17
pyridine-4-carboxaldehyde	n-propylamine	1.59	-3.63
pyridine-4-carboxaldehyde	Glycine	1.20	-1.01
pyridine-4-carboxaldehyde	Alanine	0.68	1.75
pyridine-4-carboxaldehyde	Morpholine	1.51	-1.38
pyridine-4-carboxaldehyde	Piperazine	1.51	-1.38
formaldehyde	Hydrazine	0.85	-0.68
formaldehyde	Morpholine	-0.40	-2.06
formaldehyde	Piperazine	-0.37	0.43
formaldehyde	Piperidine	-0.35	0.45
formaldehyde	n-methylhydroxylamine	0.82	6.6
p-chlorobenzaldehyde	Methylamine	6.53	-0.067
p-chlorobenzaldehyde	Ethylamine	6.59	-0.33
p-chlorobenzaldehyde	Alanine	4.74	7.45
p-chlorobenzaldehyde	Piperidine	6.56	4.61

Table 2-5 (continued)

p-chlorobenzaldehyde	Morpholine	6.26	4.79
p-chlorobenzaldehyde	urea	4.76	4.75

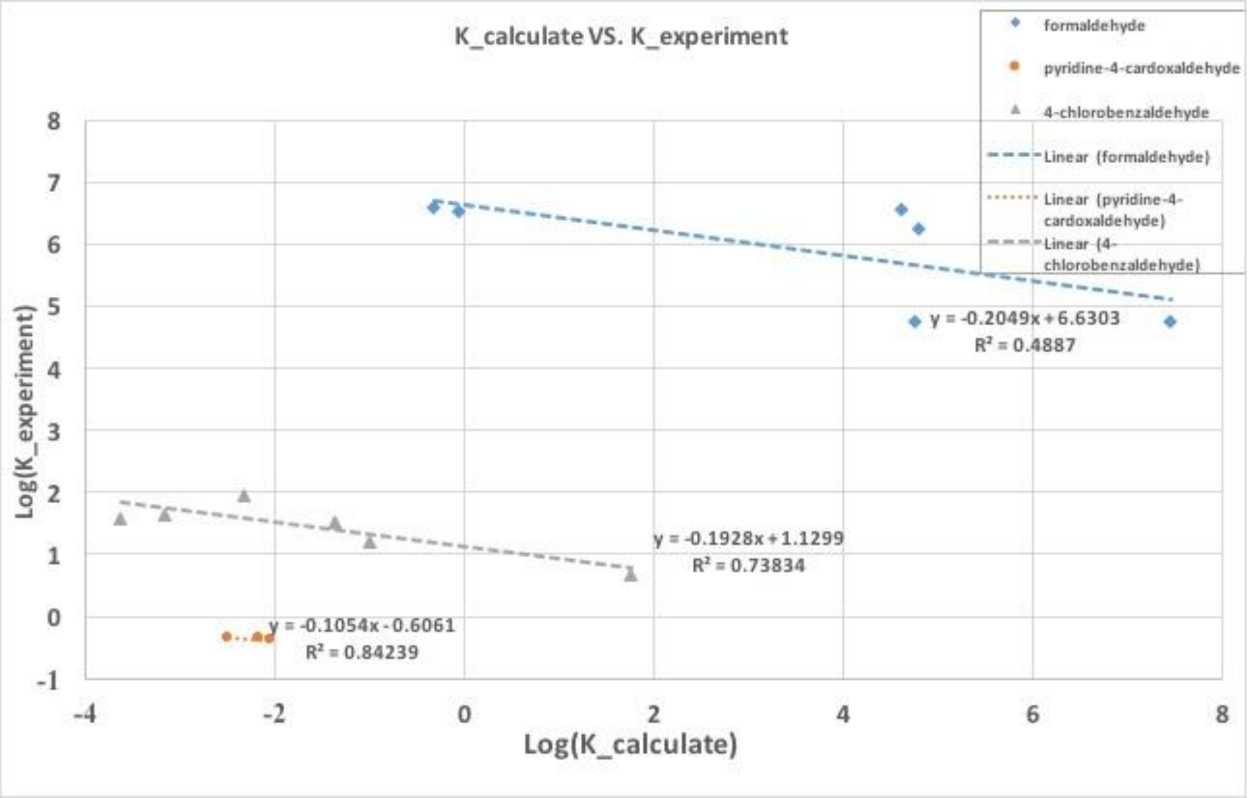


Figure 2-5 $K_{experiment}$ vs $K_{calculation}$ results

Figure 2-5 is the comparison results of experimental equilibrium constant results and calculation equilibrium constant results when choosing formaldehyde, pyridine-4-carboxaldehyde and 4-chlorobenzaldehyde as the carbonyl group. It shows that there are three separate fitted lines and there are no connections between these lines, let alone to find correlations for all points of comparison between experimental data and simulation results.

2.1.4 Conclusion

Based on the experimental data about the equilibrium constant, and compare with simulation results calculating by DFT method, no apparent correlations or connections can be found. The probability of the reason is that DFT has some corrections and approximations such as Generalized Gradient Approximations (GGA), which has been talked above, and it might be fit for this kind of circumstances. Other kind of method to connect the experimental data and simulation results of hemiaminal reactions equilibrium constant should be found and discussed.

2.2 CALCULATION BY NEURAL NETWORK (NN)

Based on the discussion above, it cannot be approached by using DFT to calculate the equilibrium constant, another method should be mentioned and discussed. Hammett and Taft created an empirical approach to calculate equilibrium constants. Hammett discussed a way to describe the relationship between reaction rate of equilibrium constant and some specific constants. The basic equation can be shown as follows:

$$\log\left(\frac{K}{K_0}\right) = \sigma\rho \qquad \text{Equation 2-15}$$

Here K is equilibrium constant and K_0 is the reference equilibrium constant, σ is the substituent constant and ρ is reaction constant. Each functional group has specific substituent constant and reaction constant. And Taft modify what Hammett did and generate a new equation that describe the reaction rate and equilibrium constant in a new way, that is called Taft equation:

$$\log\left(\frac{K}{K_0}\right) = \rho\sigma^* + \delta E_s \qquad \text{Equation 2-16}$$

Here K is equilibrium constant and K_0 is reference equilibrium constant. σ^* is called polar substituent constant, E_s is called steric constant. ρ and δ can be regarded as two different fitted parameters. Thus, for a specific reaction, pick hemiaminal reaction as an example：

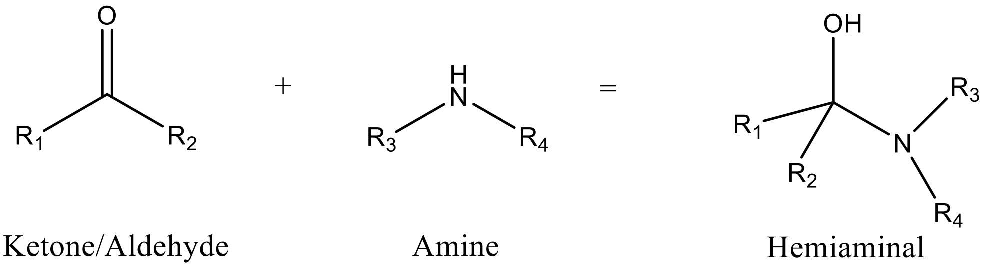


Figure 2-6 Hemiaminal reaction equation

For each hemiaminal reaction, there will be R1, R2, R3 and R4, four groups and each group has its own specific polar substituent constant σ^* and steric constant E_s. Thus, the Taft equation can be written in the following way:

$$\log\left(\frac{K}{K_0}\right) = \mathrm{F}(\mathcal{F}(\sigma^*, E_s)) \qquad \text{Equation 2-17}$$

The right-hand side expression is that there is some function between polar substituent constant and steric constant of each group and there will still be some complicated functional relationship between different groups. The simplest one can be shown as follows:

$$\log\left(\frac{K}{K_0}\right) = \sum(\rho\sigma^* + \delta E_s) \qquad \text{Equation 2-18}$$

That is a linear relationship between log(K) and the polar substituent constant and steric constant. And this is the original Hammett-Taft equation. Thus, this is a method to build the relationship between the calculation equilibrium constant and experimental equilibrium constant. The key point is to find structure of the the expression of right hand side of the equation:

$$\log\left(\frac{K}{K_0}\right) = \mathrm{F}(\boldsymbol{\mathcal{F}}(\boldsymbol{\sigma}^*, \boldsymbol{E_s})) \qquad \text{Equation 2-19}$$

Here, to introduce a method to find the expression $\mathrm{F}(\mathcal{F}(\sigma^*, E_s))$, called neural network. Neural network is a computational or mathematical model that its structure and function are similar to living neural systems. Neural network can be used as to approximate a function and it is a very good tool to do non-linear regression approximation. Neural network toolbox in MATLAB can act as a good tool to do neural network calculation. The procedure of neural network in MATLAB is shown in figure 2-7.

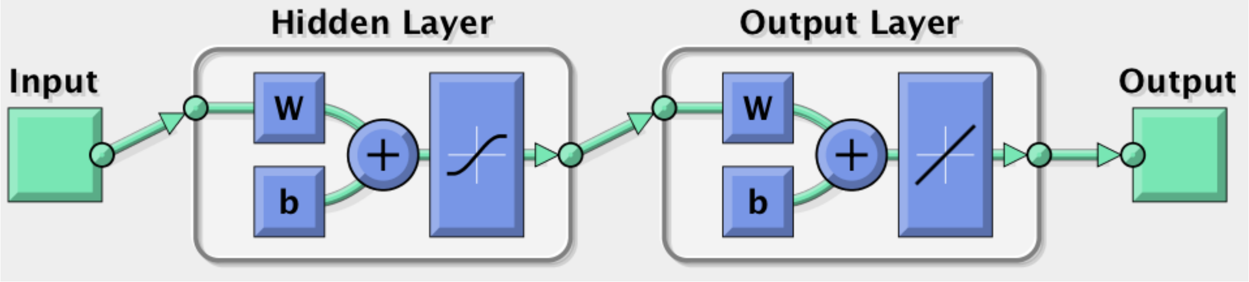


Figure 2-7 Procedure of neural network in MATLAB

First, list some different groups of data as the input. In hemiaminal reaction example, there are 8 different variables. (polar substituent constant and steric constant for each functional group, and there are R1, R2, R3 and R4, four groups) Here, the experimental data discussed above are treated as the input. And then do the neural network training, it is that randomly choose some groups of data as the training data, find the weight and bias among the different variables (shows in the hidden layer) and then use the left data as the testing data to validate and test the accuracy of the training result model.

After training and validating, the model of neural network can be used to test other hemiaminal reactions, that is to do a screening search of different kinds of hemiaminal reactions and then find one or some reactions with equilibrium constant in a reversible scope.

Here is the preparation of to do the screening. The following table shows some properties such as mass weight and boiling point of all the candidates of amines and ketones waiting to choose as the reactants of hemiaminal reactions.

Table 2-6 Mass weight and boiling point of some amines (from www.chemspider.com)

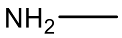
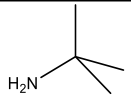
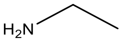
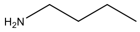
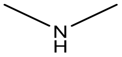
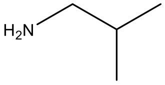
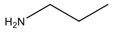
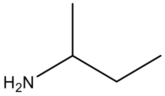
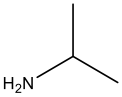
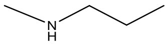
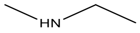
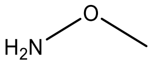
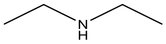
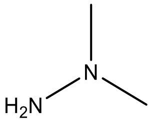
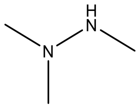
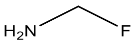
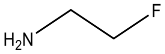
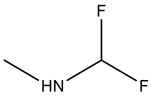
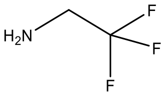
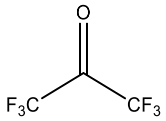
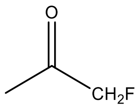
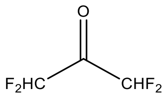
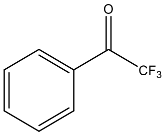
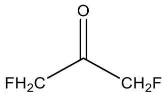
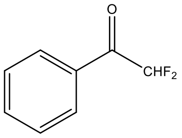
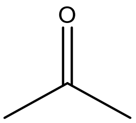
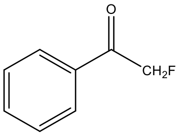
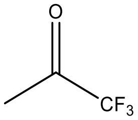
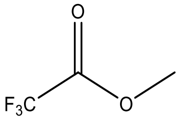
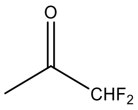
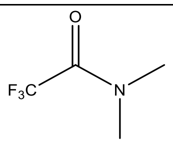
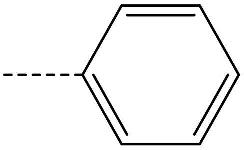
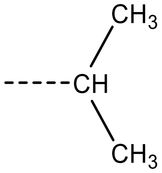
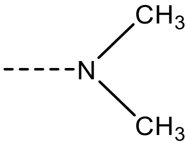
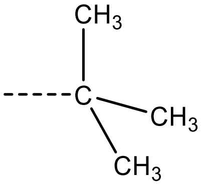
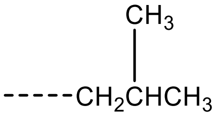
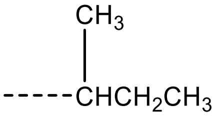
Amine	Mass weight	BP(℃)	Amine	Mass weight	BP(℃)
	31	49		73	44
	45	38		73	76
	45	60		73	67
	59	49		73	63
	59	33		73	62
	59	33		47	49
	73	36		60	61
	74	49		49	32
	63	52		81	10
	99	36			

Table 2-7 Mass weight and boiling point of some ketones (from www.chemspider.com)

Ketone	Mass weight	Boiling point	Ketone	Mass weight	Boiling point
	166	105		76	75
	130	61.8		174	165
	94	101		156	181
	58	56		138	242
	112	21		128	43
	94	46		141	135

Based on these amines and ketones, randomly choose one component from Table 2-6 and choose one component from Table 2-7, there will be 228 different reactions and all of the equations of these 228 different reactions are listed in Appendix A. These reactions are the candidates to calculate the equilibrium constant using neural network. The following table shows the polar substituent constants and steric constants of all functional groups needed to do neural network.

Table 2-8 Polar substituent constant and steric constant of some functional groups [47]

Group	σ^*	E_s	Group	σ^*	E_s
-----CF_3	2.85	-2.40	-----H	0.49	0
-----CHF_2	2.01	-1.44	-----CH_2CH_3	-0.1	-1.31
-----CH_2F	1.1	-1.32	-----$CH_2CH_2CH_3$	-0.12	-1.43
-----CH_3	0	-1.24	-----OCH_3	1.77	-0.55
	0.6	-3.82		-0.19	-1.71
-----OCH_3	1.77	-0.55	-----$CH_2CH_2CH_2CH_3$	-0.13	-1.63
	1.16	-1.71		-0.3	-2.78
-----CH_2CH_2F	0.39	-1.31	-----CH_2CF_3	0.92	-2.36
 -----$CH_2\overset{\overset{CH_3}{\vert}}{C}HCH_3$	-0.13	-2.17	 -----$\overset{\overset{CH_3}{\vert}}{C}HCH_2CH_3$	-0.21	-2.37

The Figure 2-8 are the performance results after running neural network program. The plots show the network outputs based on 25 experimental data with respect to targets for training, validating, and test. In figure 2-8, A shows the training result of output vs. target. Here the target is the data of experimental equilibrium constant we input. The blue line is fitted line and the R value of training fitted line is 0.84645. For a perfect fit, the data should all fall along a 45degree line (the dash line in A, B, C and D), where the network outputs are equal to the targets. And figure 2-8 B shows the validation result of output vs. target. It is clear that the data in validation part is much less than in training part. It is because we use 70% of experimental data to do training and 15% to do validation and 15% to do test. In figure 2-8 B, the green line is fitted line and the R value is 0.91151. Similarly, the red line in C is the fitted line for test result of output vs. target and the R value if 0.94857. In D, the all result of this problem shows that the fitted line R value is 0.82198. For this problem, the fit is reasonably good, even though the best result is to promise all data sets have a R value larger than 0.9 or higher. However, we only have several reactions with experimental equilibrium constant data, and the neural network result is not stable and also cannot guarantee that the R values of all result data sets are over 0.9.

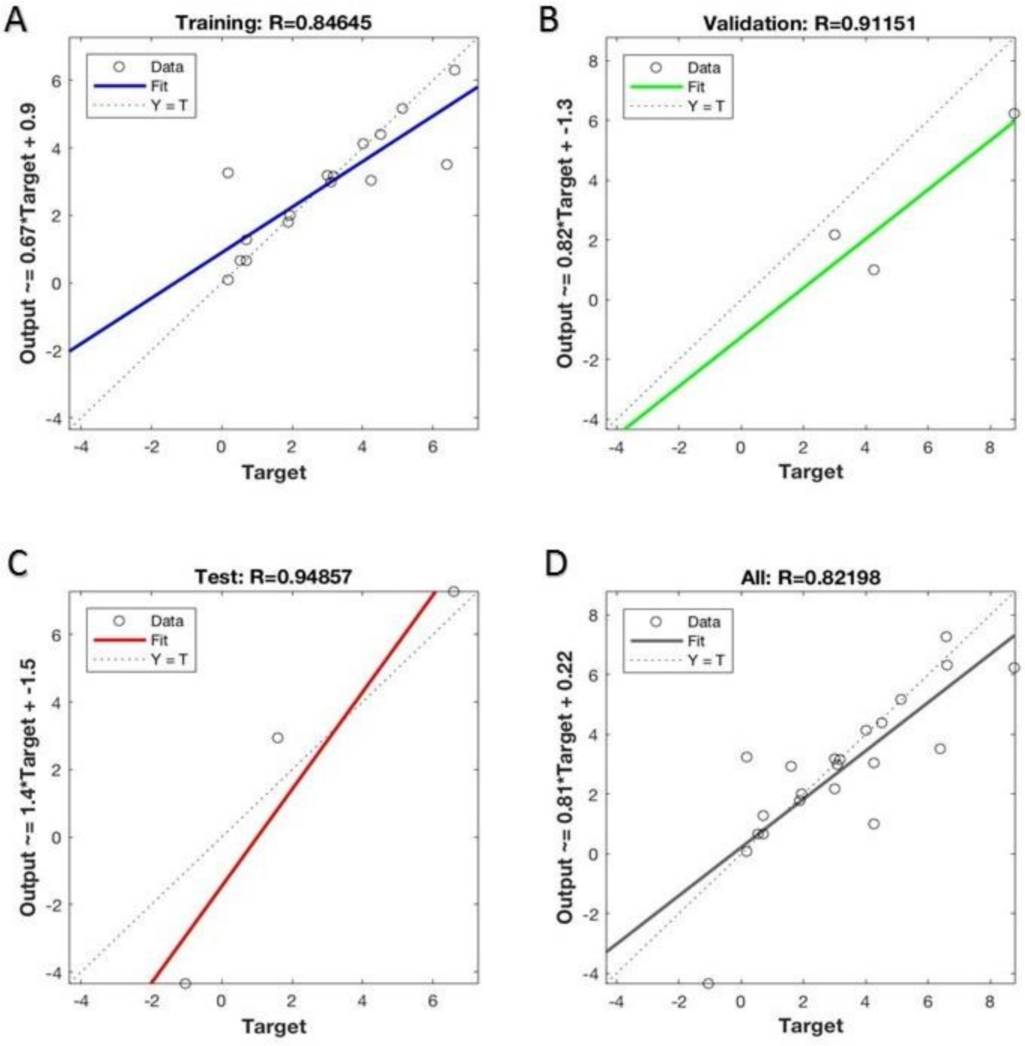


Figure 2-8 Neural network result and performance

A good way to solve this problem is to run a lot of times and then choose some results with good performances which means the result is reliable and then calculate the average. The Table 2-9 is all the numbers and equations of the reactions which equilibrium constant is between 0.1 and 10.

Table 2-9 Reactions with equilibrium constant between 0.1 to 10

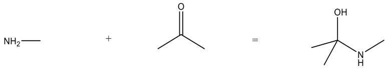
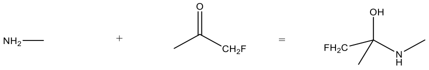
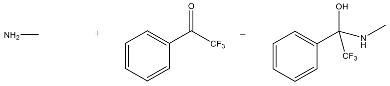
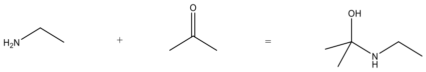
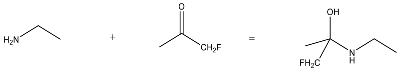
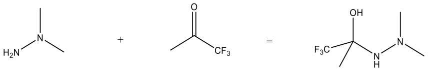
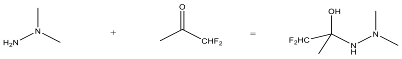
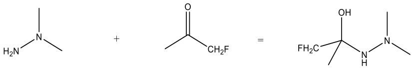
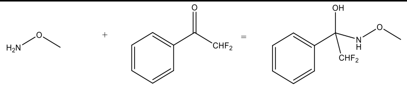
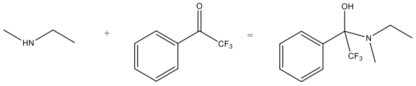
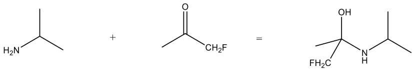
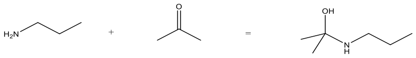
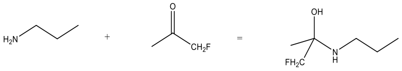
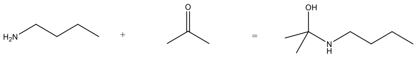
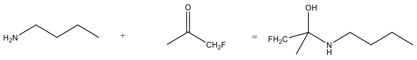
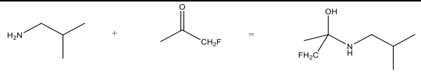
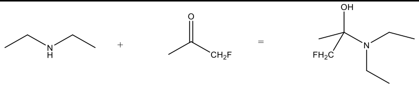
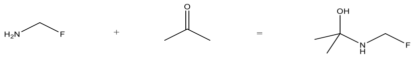
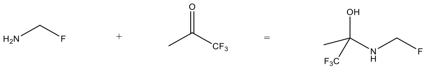
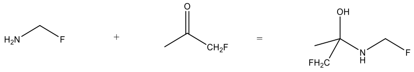
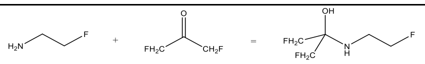
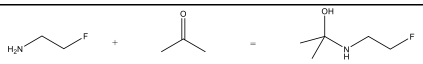
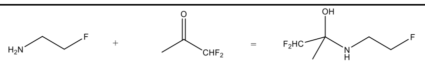
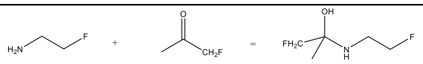
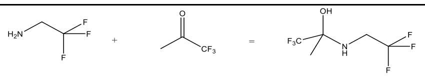
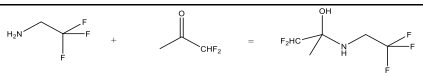
No.	Reaction	K_{eq}	No.	Reaction	K_{eq}
4		0.72	7		0.90
8		4.97	16		1.35
19		1.39	53		0.34
54		5.51	55		0.59
69		3.03	80		2.72
91		4.31	100		2.45
103		1.76	112		2.47
115		6.53	151		5.97
176		2.82	196		2.03
197		2.86	199		0.86

Table 2-9 (continued)

207		3.03	208		0.59
210		1.35	211		0.74
221		0.44	222		1.64

These reactions are the candidates that can be put into the chemical heat pump. The next step is to determine the vapor pressure vs. temperature of the reactants and products in these reactions. Based on the discussion above, two of the requirements of the hemiaminal reactions in the chemical heat pump are the reaction should be reversible and the reactants should be volatile (boiling point less than 373K). Thus, it is necessary to check the boiling point and the vapor pressure to do a further filter of the reactions above.

2.3 VOLATILITY

There are two steps to check the volatility of the components. The first step is to do a coarse filter using the boiling point. The second step is using Aspen plus to simulate and calculate the relationship between the vapor pressure and the temperature.

After sorting the boiling point of the amines we choose and list them from low temperature to high boiling point temperature:

Table 2-10 Boiling points of different amines

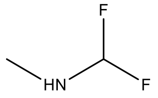
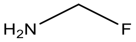
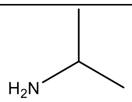
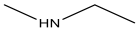
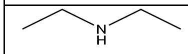
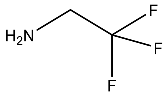
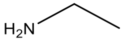
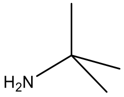
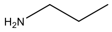
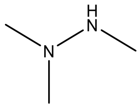
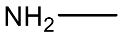
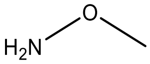
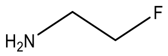
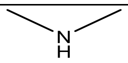
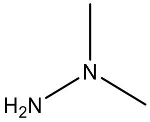
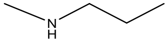
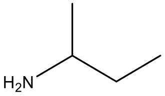
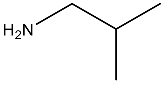
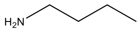
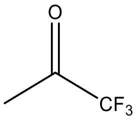
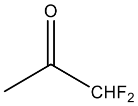
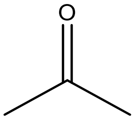
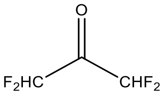
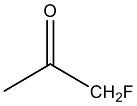
Amine	Name	BP(℃)
	1,1-difluoro-N-methylmethanamine	10
	1-fluoromethanamine	32
	2-aminopropane	33
	ethylmethylamine	33
	diethylamine	36
	trifluoroethylamine	36
	ethylamine	38
	tert-butylamine	44
	propylamine	49
	1,1,2-trimethylhydrazine	49
	methylamine	49
	methoxyamine	49
	2-fluoroethylamine	52
	dimethylamine	60

Table 2-10 (continued)

	1,1-dimethylhydrazine	61
	methyl-N-propylamine	62
	sec-butylamine	63
	isobutylamine	67
	n-butylamine	76

And then sort the boiling point of the ketones we choose and list them from the low temperature to high boiling point temperature under 100℃:

Table 2-11 Boiling points of different ketones (under 100℃)

Ketone	Name	BP(℃)
	trifluoroacetone	21
	difluoroacetone	46
	acetone	56
	1,1,3,3-tetrafluoroacetone	61.8
	fluoroacetone	75

Next step is to choose some reactions and calculate the vapor pressure of the components under different temperature and then use the equilibrium constant result to run the process design in Aspen Plus. It is good to choose some typical reactions to test the vapor pressure and then do the process design. We can calculate vapor pressure vs. temperature using built in tools in Aspen Plus. Among these reactions, there are three typical reactions, they are reaction No.4 methylamine + acetone, reaction No.54 1,1-dimethylhydrazine + difluoroacetone and reaction No.69 methoxyamine + 2,2-difluoroacetophenone. The reason why these three are typical is that the equilibrium constant of reaction No.4 is 0.74 exactly and equilibrium constant of reaction No.54 is 5.51 which is very large among all of these reactions. What's more, it is the representativeness of these components of the reaction No.4, No.54 and No.69. the components in reaction No.4 is quite simple, reaction No.69 has a large, ketone 2,2-difluoroacetophenone.

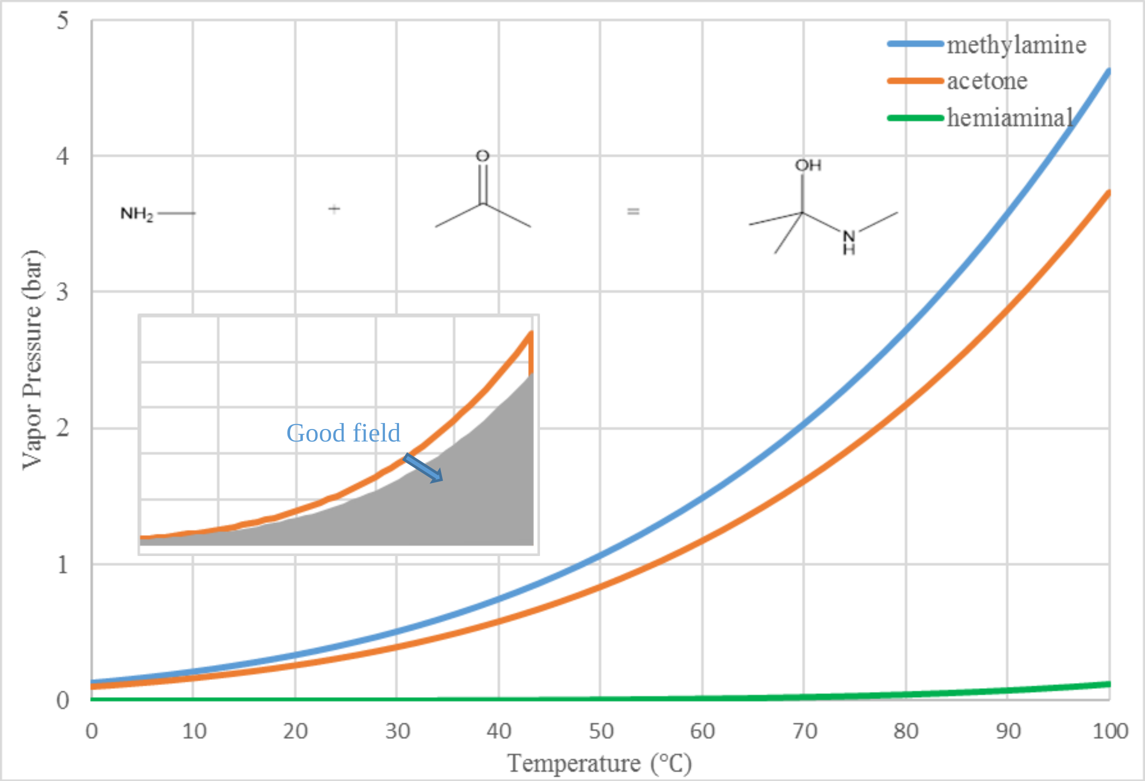


Figure 2-9 Vapor pressure vs. temperature of reaction No.4

Figure 2-9 shows the relationship between the vapor pressure and temperature of reaction No.4. It is clearly that methylamine and acetone are both volatile which means they can easily be vaporized. On the other hand, the hemiaminal is not volatile. Furthermore, the vapor pressures are almost the same for methylamine and acetone when temperature goes up. It is good because it means as a specific temperature and pressure, if methylamine is a vapor phase then acetone is also a vapor. At this point, it can be a good fit for the heat pump of hemiaminal reactions. Because in the lower temperature environment, as it has been discussed in Section 1.4, to vaporize amine and ketone can suck more heat from the low temperature environment and then vapor of amine and ketone will go to the high temperature part and regenerate hemiaminal. Thus, if the amine and ketone are both volatile and have the similar vapor pressure, it is easier to control based on changing pressure and temperature. Therefore, there is an area called "good field" in the small figure at the left-bottom corner of the Figure 18. In this area, both temperature and pressure can satisfy the situation that both amine and ketone can be vaporized except hemiaminal.

Thus, if there is a figure contains vapor pressure vs. temperature of amine, ketone and hemiaminal, the larger the "good field" is, the easier to control to vaporize amine and ketone without vaporizing hemiaminal.

In Figure 2-10, the reaction is No.54, which is 1,1-dimethyhydrazine + difluoroacetone. It is clearly that the 1,1-dimethyhydrazine and difluoacetone are both volatile, even though their vapor pressures are not the same when changing the temperature. The "good field" is not as large as the one in reaction No.4, but it can still work if changing the pressure and temperature in order to only vaporize amine and ketone. As a contrast, in Figure 2-11, when the reaction is No.69, which is methyoamine + 2,2-difluoroaceophenone. It is clearly that both hemiaminal and 2,2-

difluoroacephenone are not volatile. Therefore, it is not easy to vaporize both the amine and 2,2-difluoroaceophenone when change the pressure and the temperature.

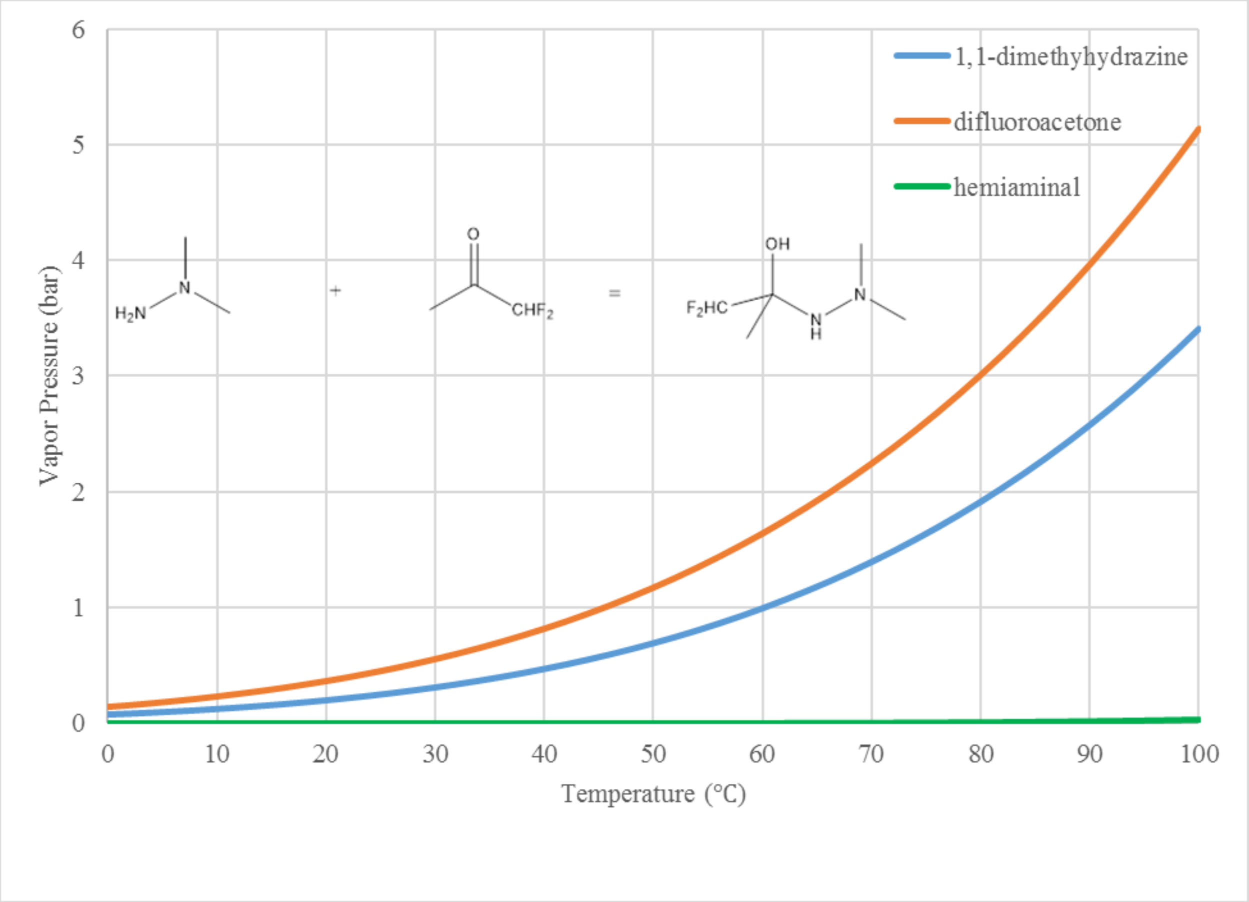


Figure 2-10 Vapor pressure vs. temperature of reaction No.54

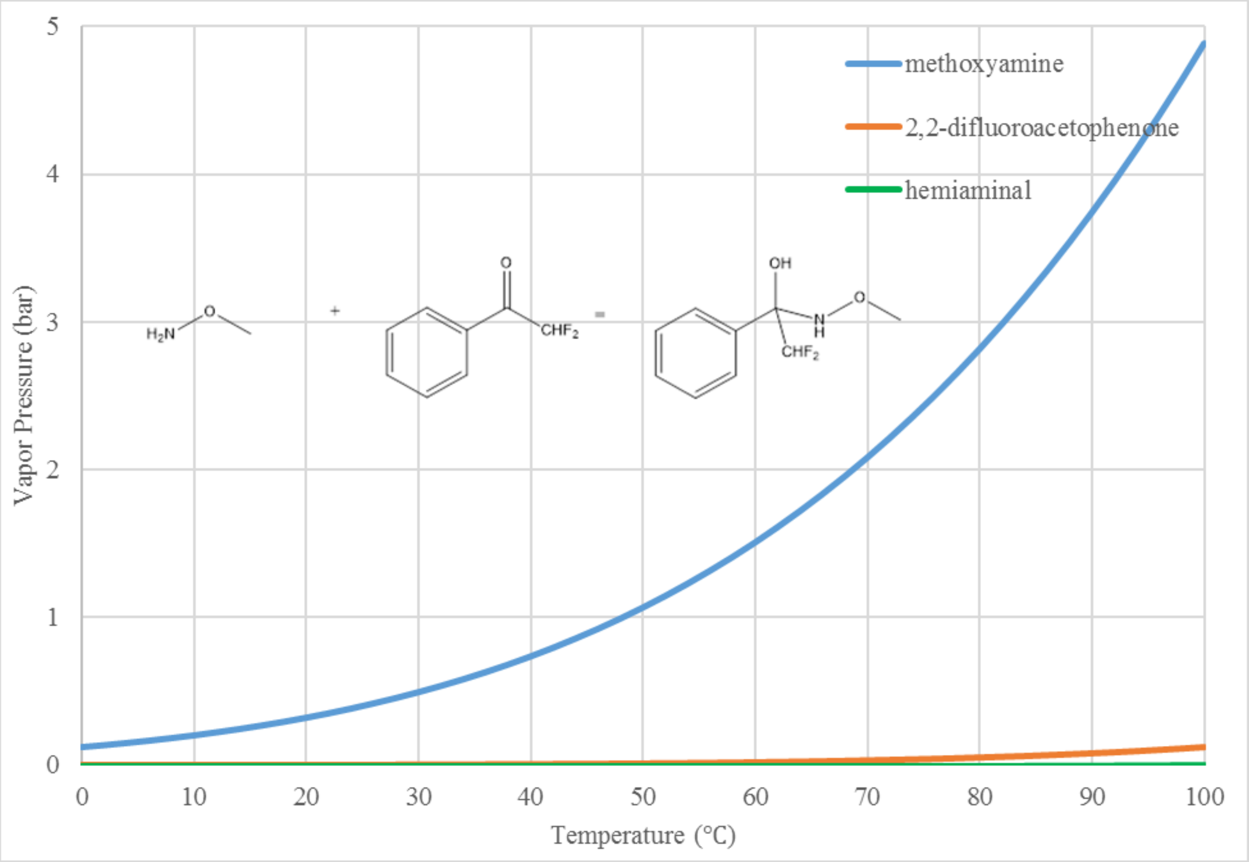


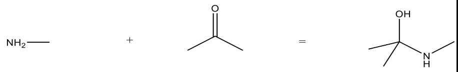
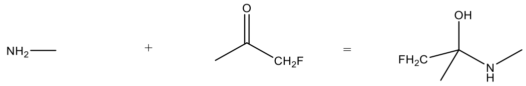
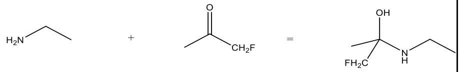
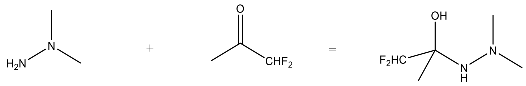
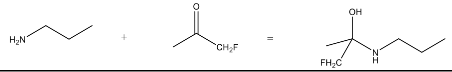
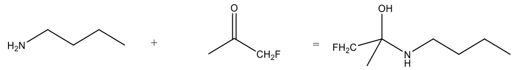
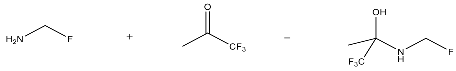
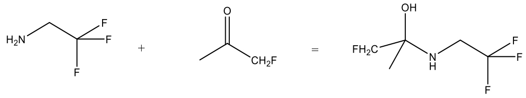
Figure 2-11 Vapor pressure vs. temperature of reaction No. 69

To sum up, in order to filter and find the reactions which can possibly run in the process simulation, the reactants, amine and ketone, should be volatile and the product hemiaminal should not be volatile. Only in this way can the amine and ketone be vaporized while the hemiaminal is still mostly liquid.

2.4 PROCESS DESIGN IN ASPEN PLUS

After the calculation of equilibrium constant by neural network and boiling point and vapor pressure calculation, we filtered the 228 hemiaminal reactions and got 23 candidates and they are listed in Table 2-9. Based on the component boiling point and the equilibrium constant of the reaction, 8 of the candidates are chosen as the typical ones to run in the Aspen Plus simulation and they are listed in Table 2-12.

Table 2-12 Reactions run in the Aspen Plus V8.4

No.4		No.7	
No.19		No.54	
No.103		No.115	
No.197		No.223	

2.4.1 Set up a simulation in Aspen Plus V8.4

Next step is to set up and run Aspen simulation based on the equilibrium constant calculated by neural network. In the Properties part, the first is to define a set of components, such as amine, ketone and hemiaminal and then define the reaction: $amine + ketone \rightarrow hemiaminal$.

Choose PENG-ROB as the method and then go to Simulation part.

In order to determine what kind of essential unit should be used as the reactor of the hemiaminal reaction, it is necessary to discuss the process of the hemiaminal reaction. Based on the working principle of the CHP in new system of Figure 1-7, the process of hemiaminal reaction in CHP can be built in this way. First, hemiaminal goes into the unit one and then becomes amine and ketone:

$$hemiaminal \rightarrow amine + ketone$$

This process is endothermic which means it will absorb some heat from the low temperature environment. Then, the vaporization of the product, amine and ketone happens in this unit. Gasification of specific component is also endothermic. The vapor contains amine and ketone goes into the next unit where occurs the following reaction:

$$amine + ketone \rightarrow hemiaminal$$

This process is exothermic and finally the whole liquid flow will go back to the first unit and repeat the cycle.

To sum up, there are two phases when the reaction happens, gas phase and liquid phase and it also need to distillate the liquid mixture and separate them based on the differences in volatilities. Thus, distillation column is a good choice to be used as the unit where reaction happens. Specifically, based on the hemiaminal reactions, because there are two phases during the process of the reaction, it is good to choose RadFrac (rigorous 2 or 3 phases fractionation for a single column) as the unit in Aspen Plus. Therefore, the RadFrac named Column1 was built in the low temperature environment where $hemiaminal \rightarrow amine + ketone$ happens here and the RadFrac named Column2 was built in the high temperature environment where $amine + ketone \rightarrow hemiaminal$ happens in this part. To change the pressure in the column can achieve the feature of vaporization and liquidation, thus in Column1 the pressure can be relatively low and in Column2 the pressure can be relatively high. In order to balance the pressure between Column1 and Column2, a compressor is needed for the vapor stream and a pump is needed for the liquid steam. On the opposite direction, from Column2 to Column1, because both stream are liquid, they need a valve to rebalance the pressure.

The total process shows in Figure 2-12.

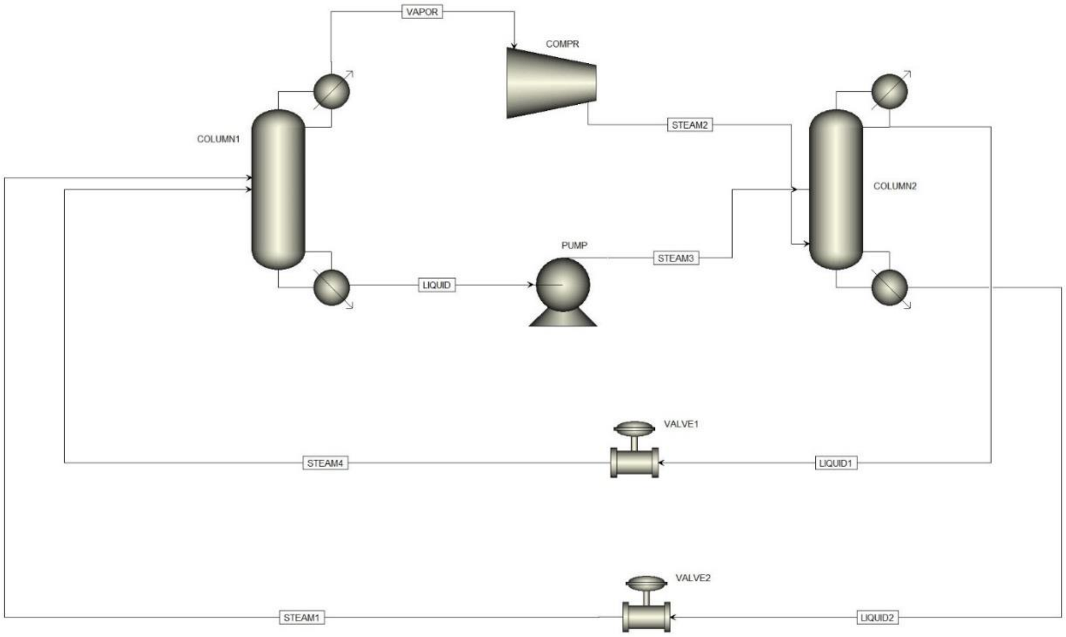


Figure 2-12 Process of CHP in Aspen plus

We use a specific reaction (amine: 1,1-dimethylhydrazine and ketone: difluoroacetone) as an example. First hemiaminal goes from stream 1 into Column1. There are two stages in Column1 (more can be added) and the stream of hemiaminal goes into stage1 and will react into 1,1-dimethylhydrazine and difluoroacetone in Column1 where the pressure is low (0.09 bar in this example). After distillation, almost all of the 1,1-dimethylhydrazine and difluoroacetone go into top stage of the column and go through compressor and then go into Column2 where the pressure is 1.4 bar. The small amount of liquid goes from the bottom of the stage and goes through the pump and then arrives Column2. There are two stages in Column2. The vapor (1,1-dimethylhydrazine and difluoroacetone) will go on the bottom stage and the liquid will go above the top stage. Then 1,1-dimethylhydrazine and difluoroacetone react and change to hemiaminal. The stream contains hemiaminal primarily, as well as 1,1-dimethylhydrazine and difluoroacetone goes back through valves to lower the pressure to the same as Column1 and goes into Column1 again. Then the cycle repeats.

2.4.2 Simulation results and conclusion

Table 2-13 shows the simulation results of Aspen Plus when choosing reaction No.4, No.7, No.19, No.54, No.103, No.115, No.197 and No.223 as the candidate reactions. The simulation results include:

- Hemi after C1: percentage of hemiaminal after the reaction in Column1.
- Hemi after C2: percentage of hemiaminal after the reaction in Column2.
- Pressure (C1): the reactor pressure in Column1.
- Pressure (C2): the reactor pressure in Column2.
- Temperature (C1): the reactor temperature in Column1.
- Temperature (C2): the reactor temperature in Column2.
- Log(K_{eq}): equilibrium constant of the reaction: $amine + ketone \rightarrow hemiaminal$.
- Heat Duty (C1): heat duty of the reboiler in Column1.
- Heat Duty (C2): heat duty of the compressor in Column2.
- Work (compressor): the net work required in compressor.
- Work (pump): the net work required in pump.
- COP: the coefficient of performance. (defined on section 1.1.2)

Table 2-13 Aspen Plus simulation results of different reactions

Reaction No. / Property	4	7	19	54	103	115	197	223
Hemi after C1 (%)	0.04	0.05	0.005	0.02	0.006	-	-	0.05
Hemi after C2 (%)	22	26	33	63	39	-	-	67
Pressure (C1)	0.1	0.1	0.2	0.09	0.09	-	-	0.1

Table 2-13 (continued)

Pressure (C2)	1.5	1.5	1.4	1.4	1.4	-	-	1.4
Temperature (C1)	0	0	5	8	8	-	-	5
Temperature (C2)	68	68	43	78	74	-	-	74
Log(K_{exp})	-0.33	-0.11	0.33	1.71	0.57	1.88	1.05	2.07
Heat duty (C1) (kW)	12.25	12.13	14.12	10.33	11.40	-	-	1.16
Heat duty (C2) (kW)	-17.06	-16.95	-17.36	-15.10	-16.16	-	-	-5.65
Work (compressor)	4.82	4.82	3.23	4.76	4.76	-	-	4.49
Work (pump)	0.0003	0.0003	0.0003	0.0002	0.0003	-	-	0.0003
COP	2.54	2.52	4.37	2.17	2.40	-	-	0.26

From the Table 2-13, there is not a substantial difference among the results for percentage of hemiaminal after Column1. As a comparison, the percentage of hemiaminal after Column2 shows a large difference between different reactions. For example, after the regeneration of Column2, the percentage of hemiaminal is 22% for reaction No.4 (amine: methylamine, ketone: acetone). However, the percentage of hemiaminal after Column2 is 63% for reaction No.63 (amine: 1,1-dimethylhydrazine, ketone: difluoroacetone). It is because the equilibrium constant of the hemiaminal reaction: $amine + ketone \rightarrow hemiaminal$ is larger in reaction No.54 than in reaction No.4. Even though to produce more hemiaminal also means the equilibrium constant will be lower for opposite direction, the amine and ketone production direction, the reaction can still produce almost 100% amine and ketone because of the gasification of amine and ketone. To vaporize the amine and ketone can push the reaction to go further. This illustrates why all the reactions have the similar percentage of hemiaminal after Column1.

One of the ways to vaporize components is to make the pressure lower in the reactor. Thus, all the reactions in Table 2-13 have a relatively low pressure in Column1, much lower than 1 bar. On the contrary, in order to liquify the components, one should raise the pressure in the reactor. That’s why the pressures in Column2 of different reactions are all higher than 1bar. And due to the pressure difference (ΔP) between Column1 and Column2, it is necessary to add a compressor for the vapor steam and to add a pump for the liquid steam between Column1 and Column2.

Temperature in Column1 should be lower than 10℃ because the ambient temperature is 10℃ and Column1 is a low temperature environment and it will be endothermic to absorb heat from the environment. On the contrary, the temperature in Column2 should be higher because the Column2 is a high temperature environment and it will be exothermic to release heat back to environment.

To judge a performance of a heat pump, it is typical to use COP (coefficient of performance) as a standard. As it is discussed in Section 1.1.2, the COP equation can be written in the following way:

$$\boldsymbol{COP} = {}^{\boldsymbol{Q}}/_{\boldsymbol{W}} \qquad \text{Equation 2-20}$$

where Q is useful heat from the system, and W is the work or heat input required by the system. In the system which is simulated in Aspen Plus, the heat Q is the heat duty of reboiler. The heat duty of the reboiler is positive means that it is endothermic and it is the Q part in the equation. The work W is the work required which means the sum of the work of compressor and the work of pump. Thus, the COP equation can be written in this way in this system:

$$COP = \frac{Heat\ Duty\ of\ reboiler}{W_{compressor} + W_{pump}}$$ Equation 2-21

And it is clearly that the W_{pump} can be neglected compared with $W_{compressor}$, therefore, the equation is now:

$$COP = \frac{Heat\ Duty\ of\ reboiler}{W_{compressor}}$$ Equation 2-22

From table 2-13, the COP of the whole system can reach a peak of 4.37 when the regeneration of hemiaminal is 33% and can also contain a COP of 2.17 when the regeneration of hemiaminal is 63% which is much more realistic in industrial field. And compared with the literature data about COP, which has been discussed above, the COPs of the most chemical heat pump are around 1 to 2. [17] Thus, to summarize, the chemical heat pump based on the hemiaminal reaction can have a relatively higher coefficient performance based on the process simulation and computational calculation results.

3.0 CONCLUSIONS

This thesis generated and described a new type of chemical heat pump (CHP) which is based on reversible hemiaminal reactions, and used two method, DFT and neural network method, to find the hemiaminal reactions which are reversible (the equilibrium constant is about from 0.1 to 10). We used DFT to calculate the heat of formation and Gibbs free energy of formation, and used these results to calculate the Gibbs free energy of reaction and the heat of reaction. And using equation $\Delta G^{\circ} = -\mathrm{RTln}K_{eq}$, we calculated the equilibrium constant and we used Van't Hoff equation to calculate the relationship between the equilibrium constant and temperature. However, the DFT method does not work based on the discussion. Based on the experimental data about the equilibrium constant, and compare with simulation results calculating by DFT method, no apparent correlations or connections can be found. The second method used is neural network. In this thesis paper, neural network will find the relationship between polar substituent constant and electric constant of the hemiaminal reaction components and equilibrium constant of the hemiaminal reaction.

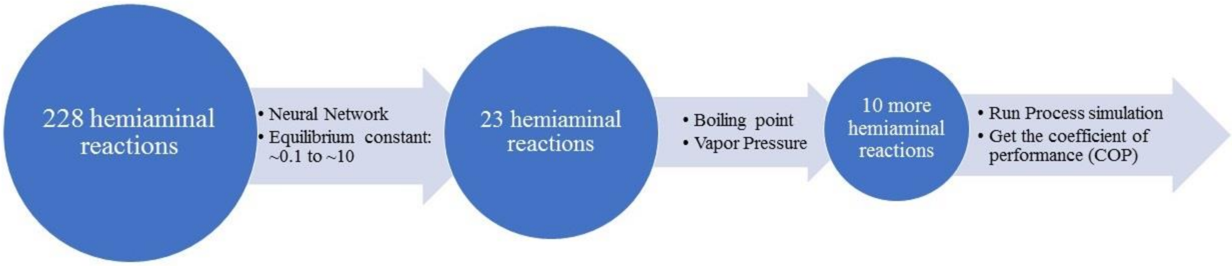


Figure 3-1 Process of the thesis paper

Thus, just as Figure 3-1 shows, a total 228 different hemiaminal reactions (combination of 19 different amines and 12 different ketones) were chosen as the candidates to do the screening using neural network. After the calculation of neural network, there are 23 hemiaminal reactions, the equilibrium constant of which are between 0.1 to 10. Among the 23 hemiaminal reactions, using boiling point and vapor pressure of the components to do a further filter, the reactions were narrowed to less than 20. Then, some of the typical ones were chosen to run in the process simulation of Aspen Plus V8.4. After the simulation of process, the coefficient of performance (COP) could be calculated and most of the reactions run in the process simulation can have a COP more than 2, which is higher than other literature results of the chemical heat pump.

To sum up, this paper generated a new idea about the chemical heat pump. That is using hemiaminal reaction as the reaction in the chemical heat pump, and the more important thing is that not only using heat of reaction of an endothermic reaction as a way to absorb heat from environment, but adding the heat of gasification of the components as a major way to absorb heat from the environment. And based on the process simulation result, the COP of the hemiaminal reaction chemical heat pump can be more than 2, which is higher than other literature results.

However, there are still more work to be done in the future. Until now, we still don't have a good method to simulate the equilibrium constant. Even though the neural network results showed much better than density functional theory, it should be mentioned that there are only 25 experimental data used as the training and validating process during the calculation of neural network, and the equilibrium constant result is calculated after the average of 11 times of different neural network training. Actually, if there are enough experimental data, the result of neural network should be stable. Thus, the results of equilibrium constant calculated by neural network until now are not 100% reliable. Thus, there are two directions in the future to solve this problem. The first is to explore and get more experimental data of the hemiaminal reactions, the second is to find a better computational modeling to simulate the equilibrium constant of the hemiaminal reaction better. Last but not the least, there is a great potential for chemical heat pump based on hemiaminal reactions in the future. It has a great possibility for this kind of heat pump used in the industrial area in the future.

APPENDIX

APPENDIX A

HEMIAMINAL REACTION EQUATIONS

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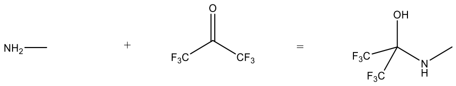
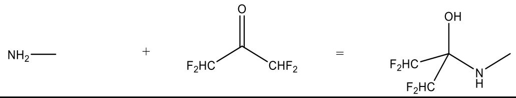
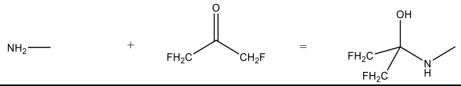
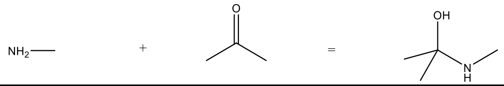
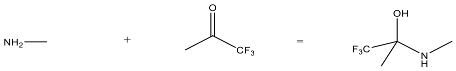
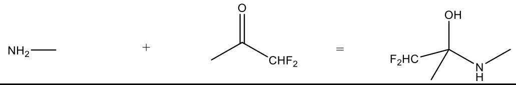
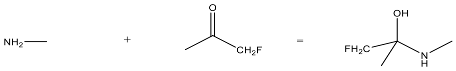
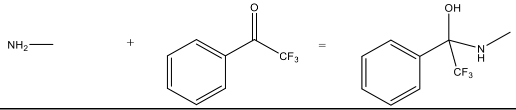
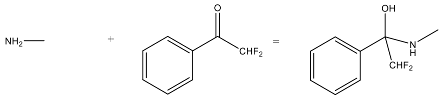
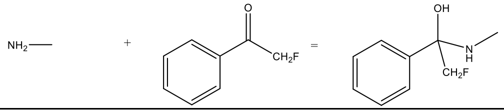
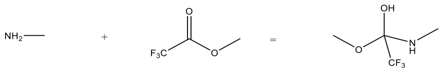
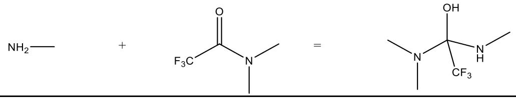
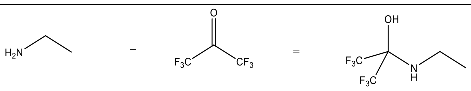
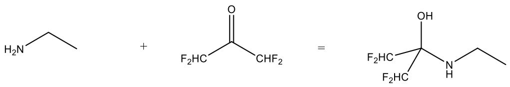
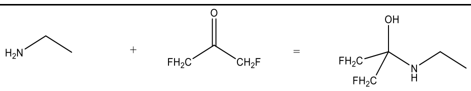
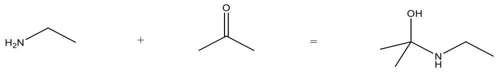
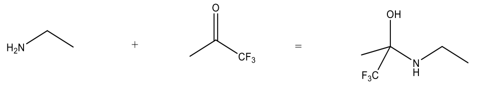
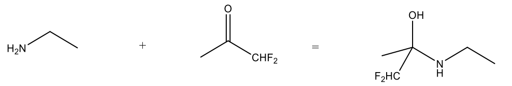
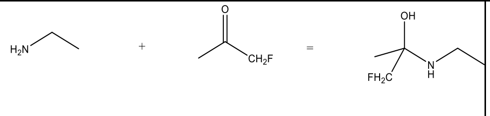
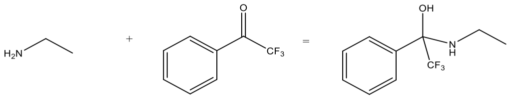
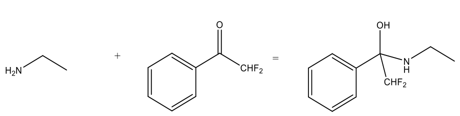
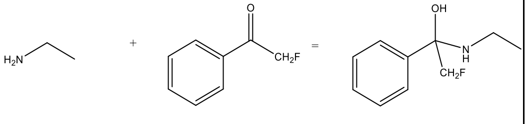
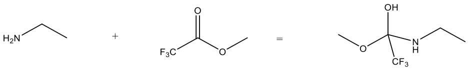
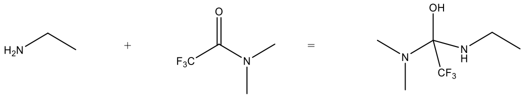
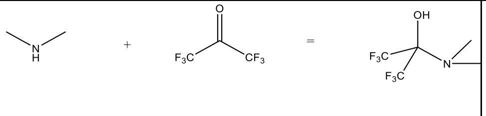
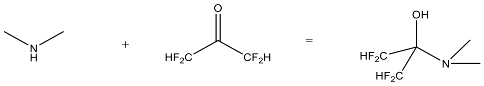
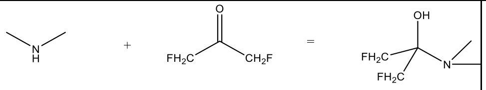
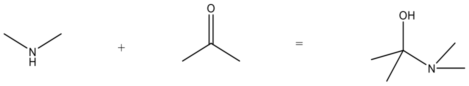
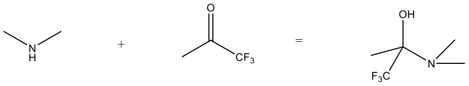
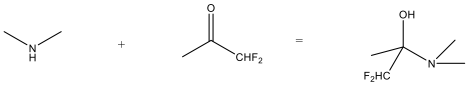
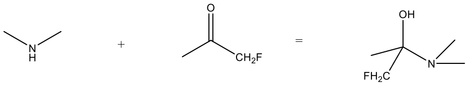
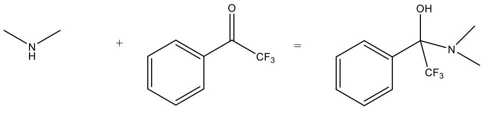
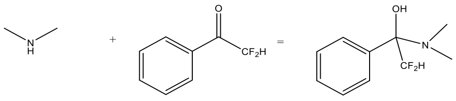
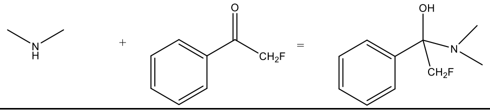
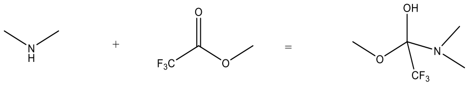
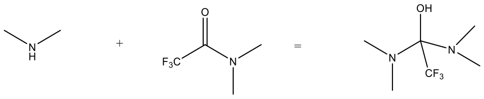
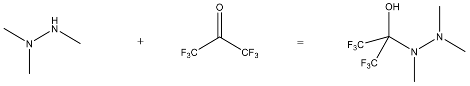
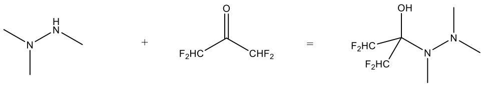
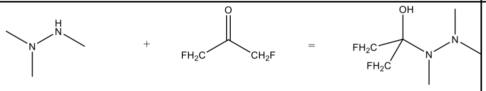
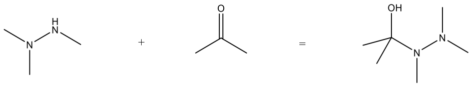
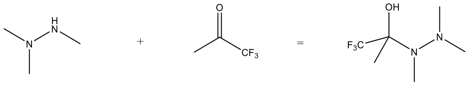
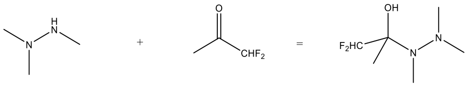
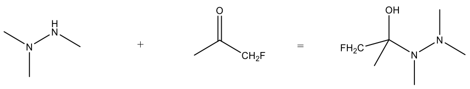
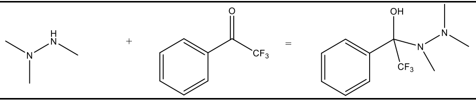
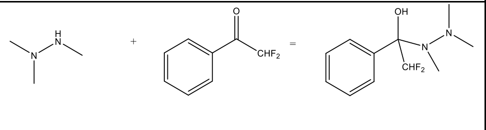
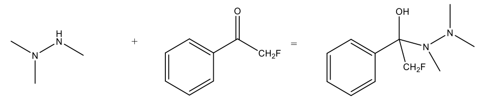
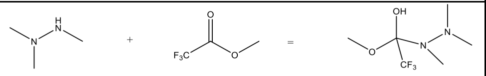
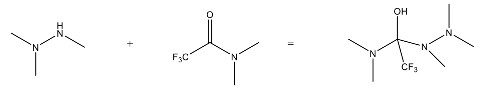
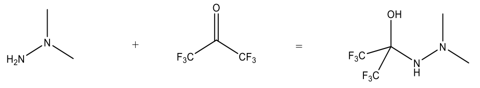
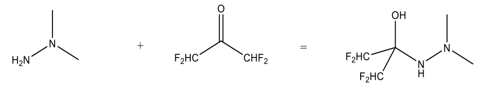
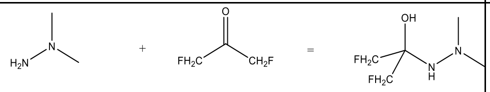
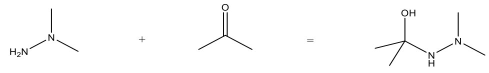
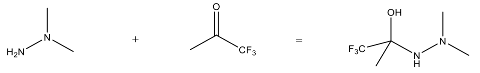
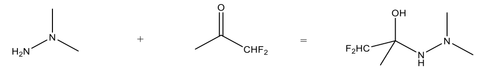
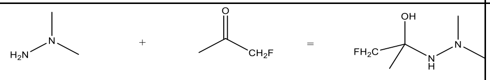
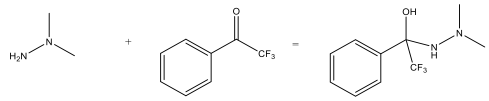
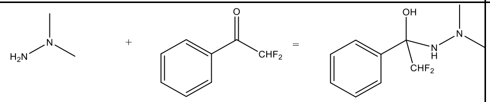
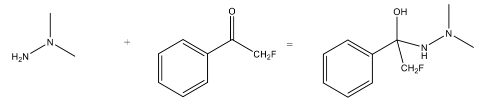
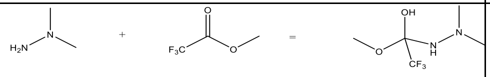
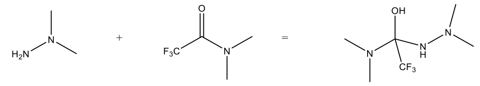
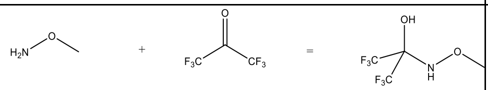
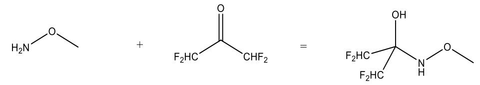
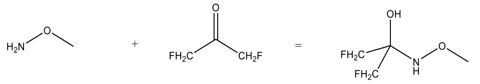
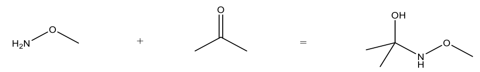
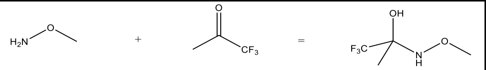
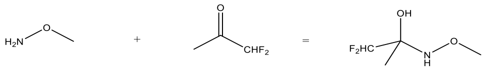
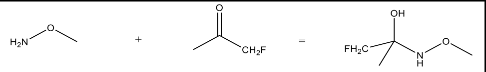
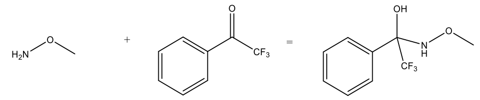
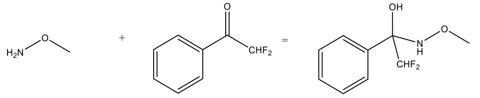
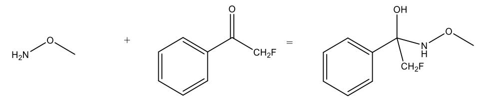
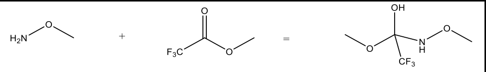
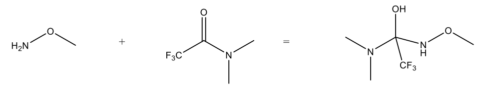
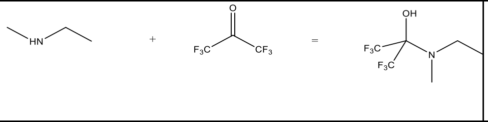
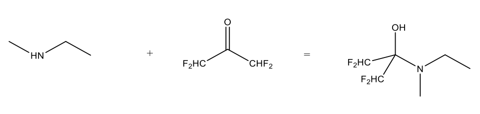
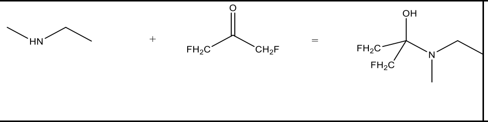
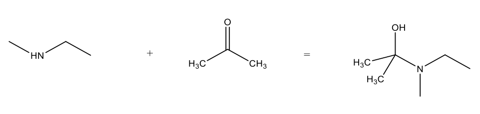
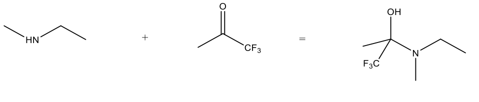
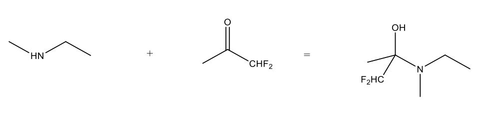
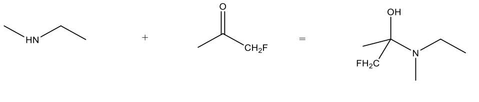
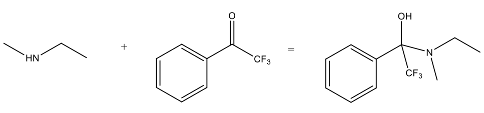
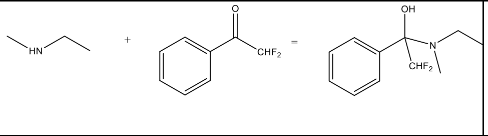
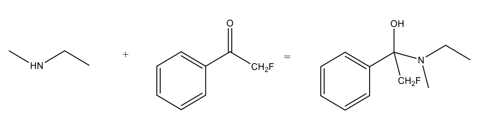
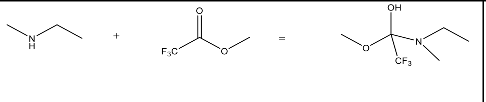
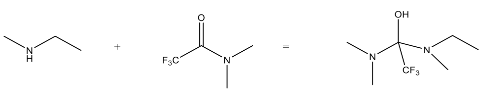
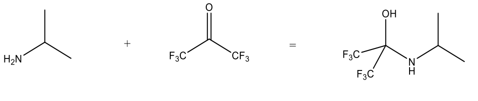
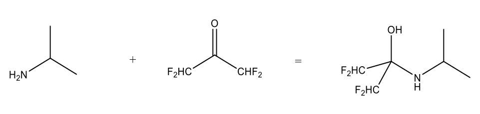
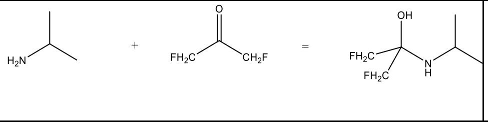
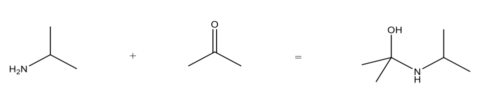
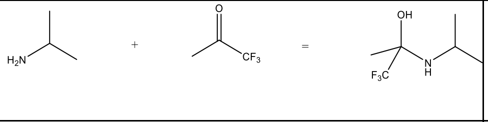
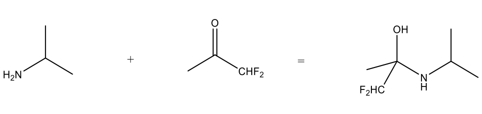
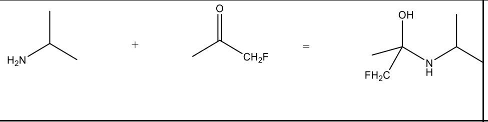
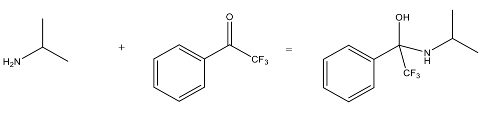
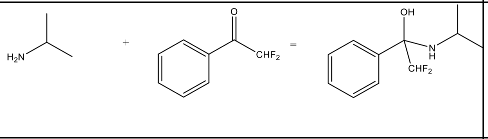
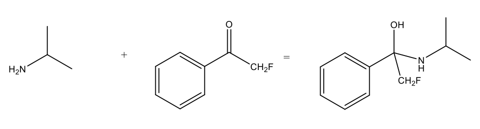
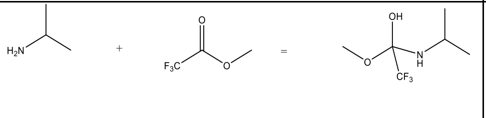
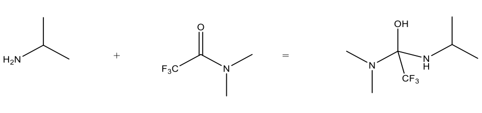
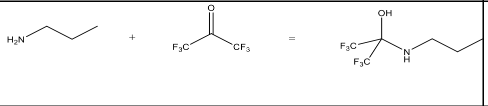
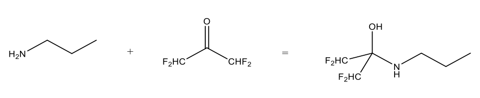
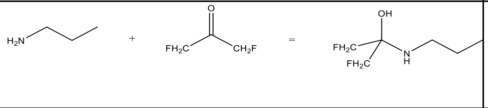
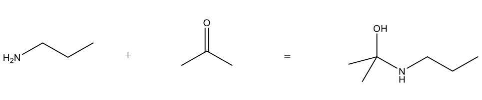
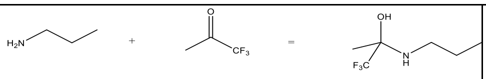
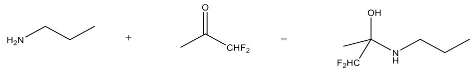
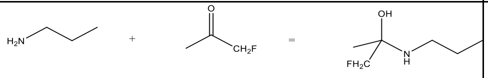
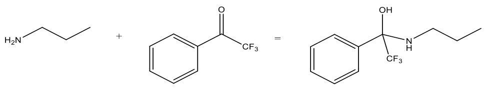
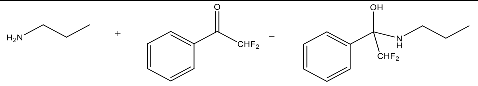
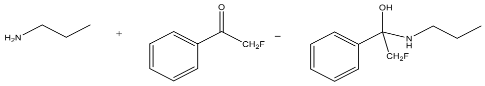
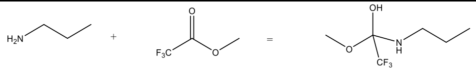
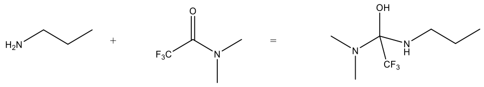
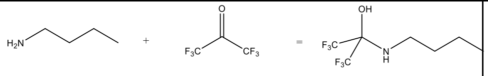
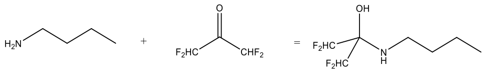
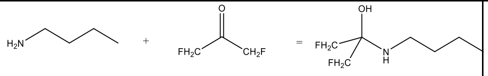
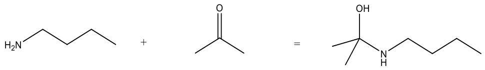
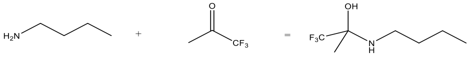
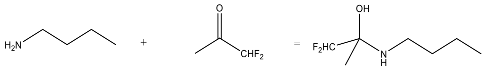
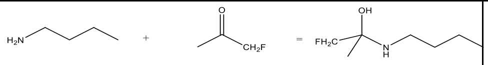
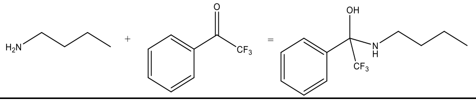
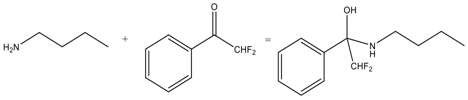
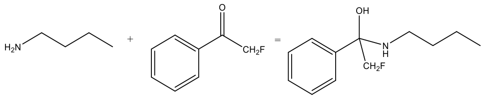
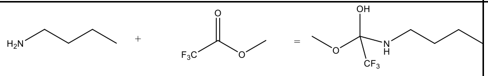
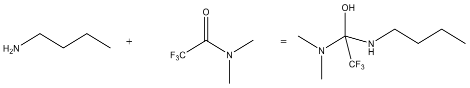
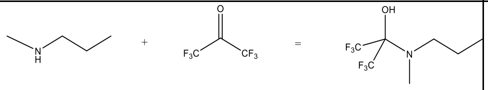
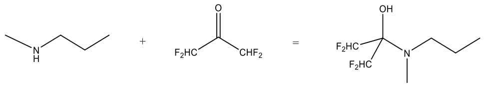
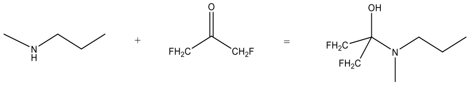
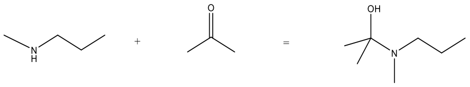
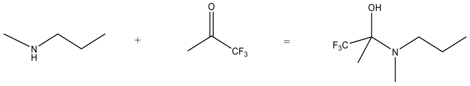
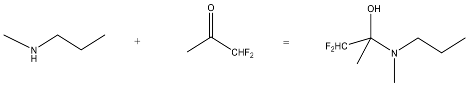
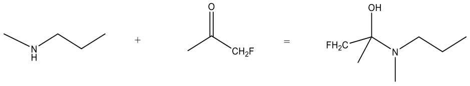
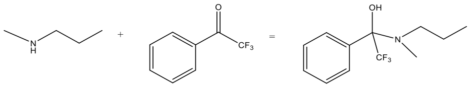
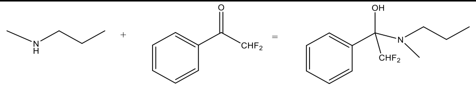
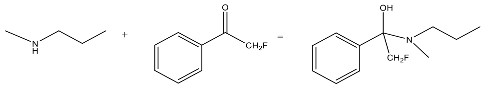
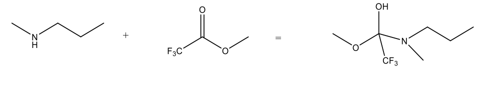
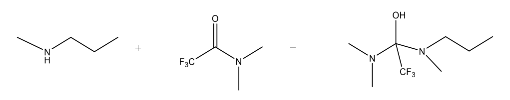
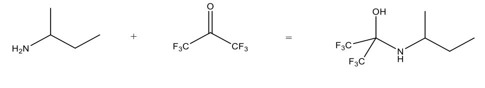
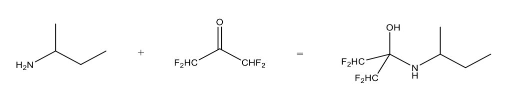
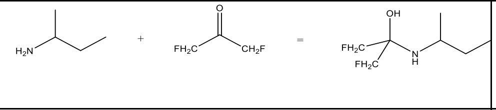
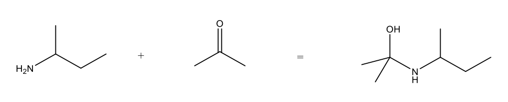
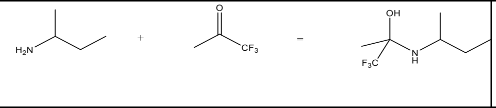
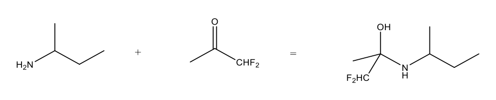
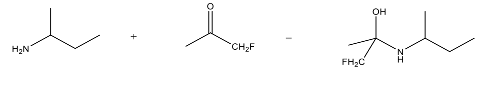
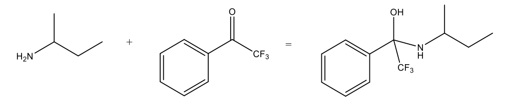
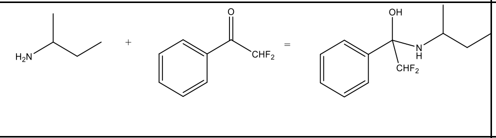
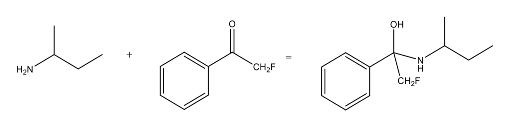
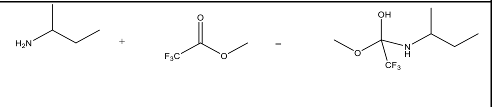
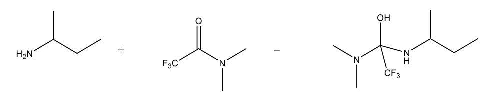
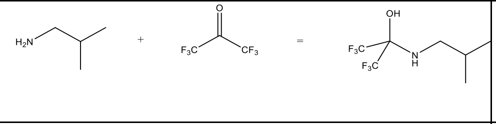
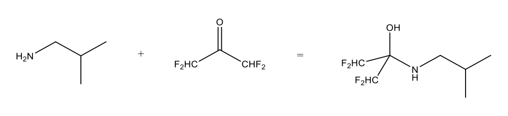
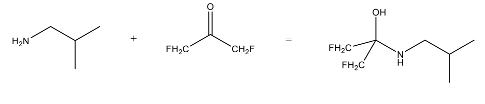
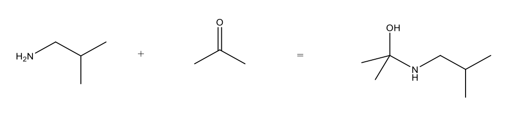
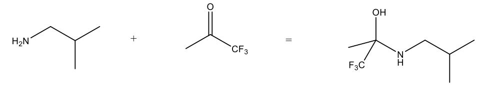
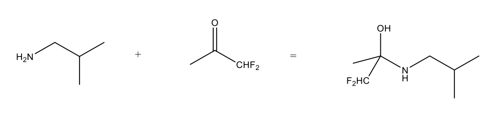
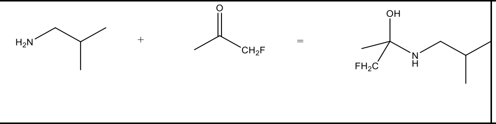
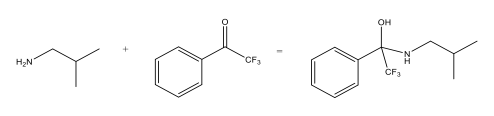
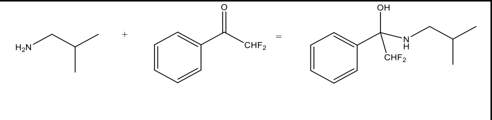
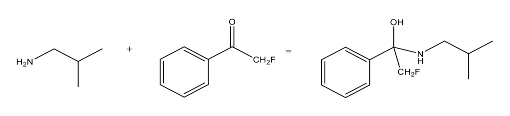
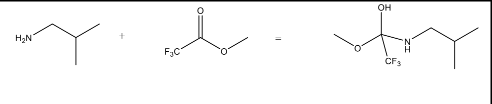
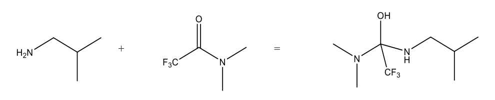
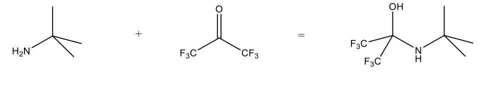
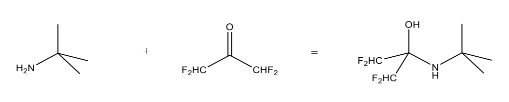
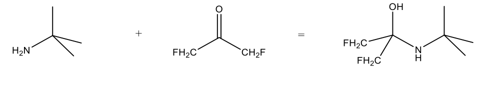
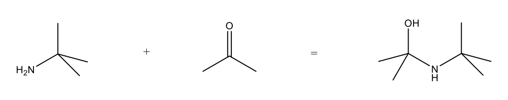
1		2	
3		4	
5		6	
7		8	
9		10	
11		12	
13		14	
15		16	

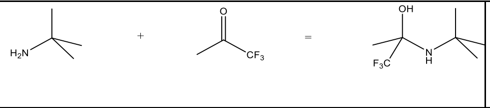
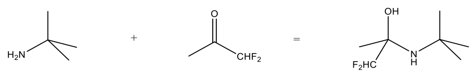
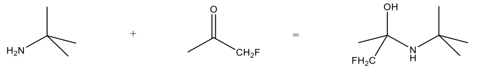
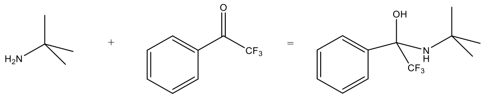
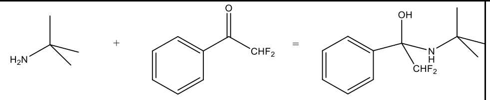
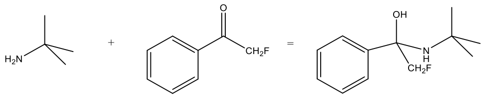
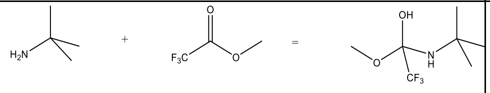
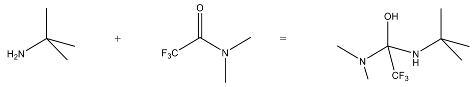
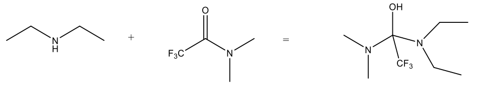
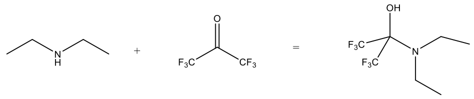
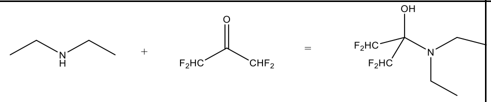
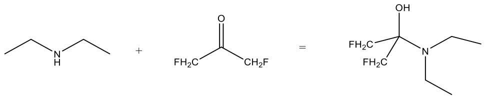
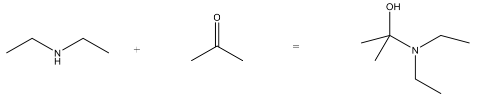
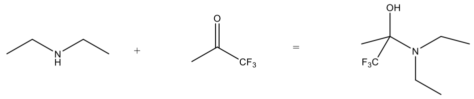
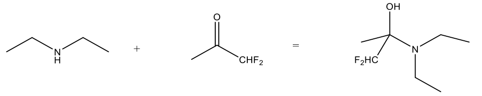
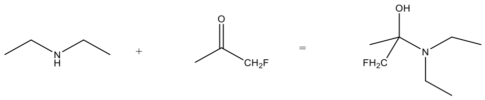
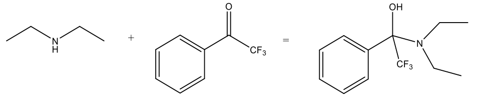
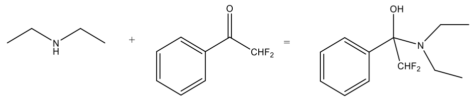
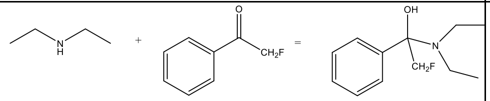
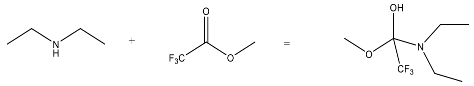
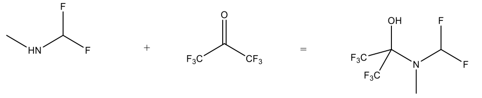
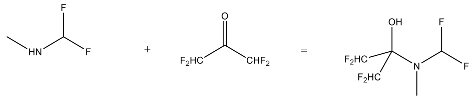
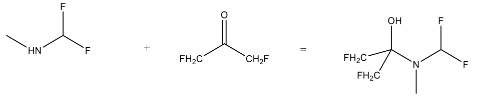
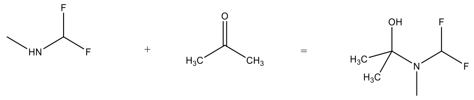
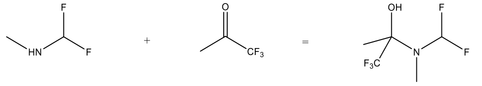
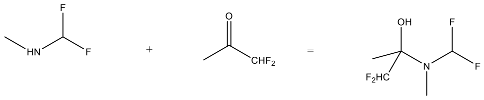
17		18	
19		20	
21		22	
23		24	
25		26	
27		28	
29		30	
31		32	
33		34	
35		36	
37		38	
39		40	
41		42	
43		44	

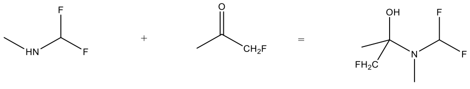
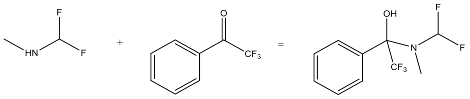
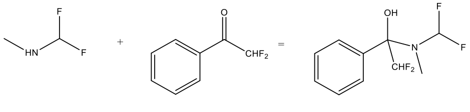
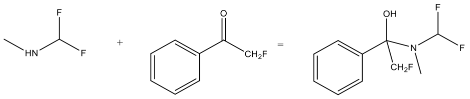
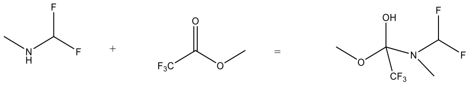
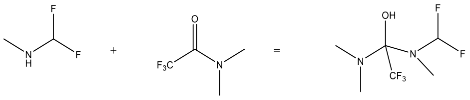
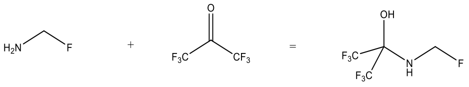
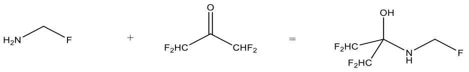
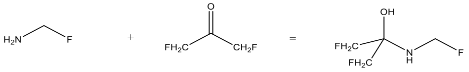
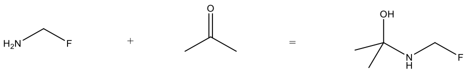
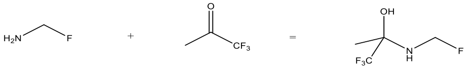
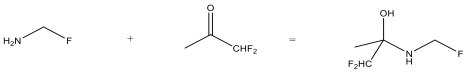
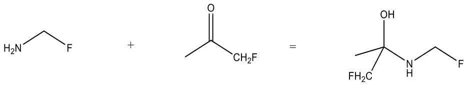
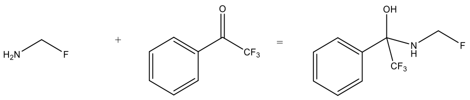
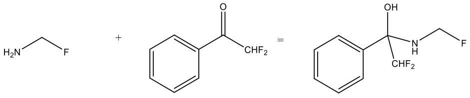
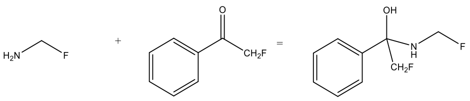
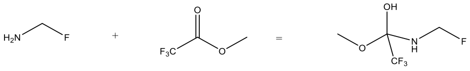
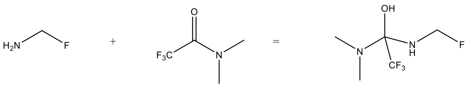
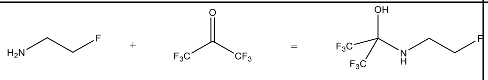
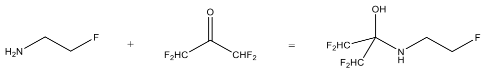
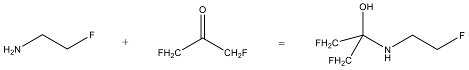
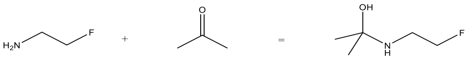
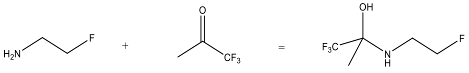
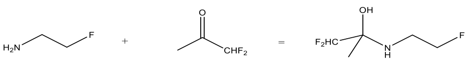
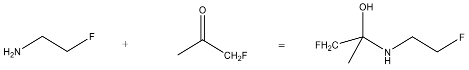
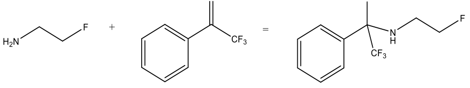
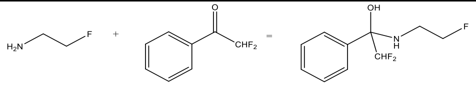
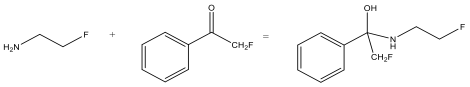
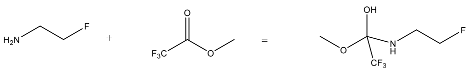
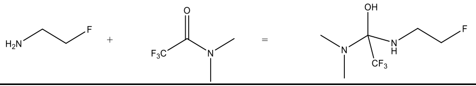
45		46	
47		48	
49		50	
51		52	
53		54	
55		56	
57		58	
59		60	
61		62	
63		64	
65		66	
67		68	
69		70	
71		72	

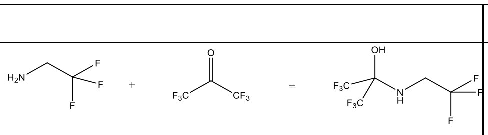
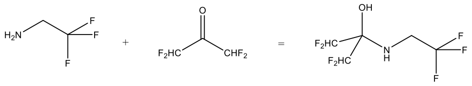
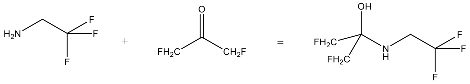
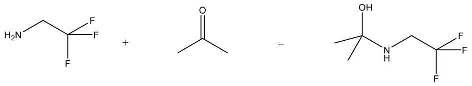
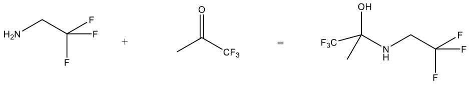
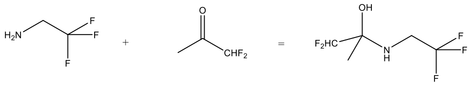
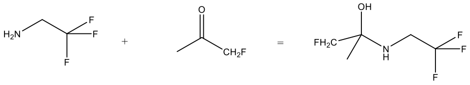
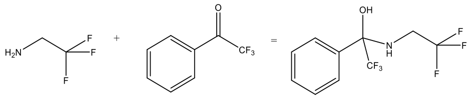
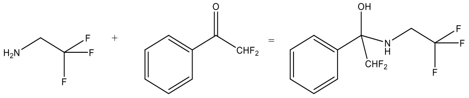
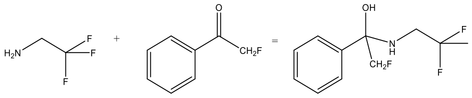
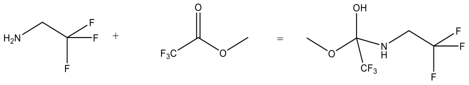
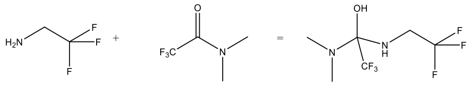
73		74	
75		76	
77		78	
79		80	
81		82	
83		84	
85		86	
87		88	
89		90	
91		92	
93		94	
95		96	
97		98	
99		100	

101		102	
103		104	
105		106	
107		108	
109		110	
111		112	
113		114	
115		116	
117		118	
119		120	
121		122	
123		124	
125		126	
127		128	
129		130	

131		132	
133		134	
135		136	
137		138	
139		140	
141		142	
143		144	
145		146	
147		148	
149		150	
151		152	
153		154	
155		156	
157		158	
159		160	

161		162	
163		164	
165		166	
167		168	
169		170	
171		172	
173		174	
175		176	
177		178	
179		180	
181		182	
183		184	
185		186	

187		188	
189		190	
191		192	
193		194	
195		196	
197		198	
199		200	
201		202	
203		204	
205		206	
207		208	
209		210	
211		212	
213		214	
215		216	

217		218	
219		220	
221		222	
223		224	
225		226	
227		228	

APPENDIX B

MATLAB CODE FOR NEURAL NETWORK

```
% This script assumes these variables are defined:
%
%   X - input data.
%   yy - target data.

x1 = [0.49 0.49 0.49 -0.1 0.49 0.49 0.49 0.49 0.49 0 0.49 0.49 0.49 0.49 -0.1 0.49 0.49 0.49 0.49 0.49 0 0.49];
x2 = [0 0 0 -1.31 0 0 0 0 0 -1.24 0 0 0 0 -1.31 0 0 0 0 0 -1.24 0];
x3 = [0.49 0 -0.1 -0.1 -0.12 -0.13 -0.17 0.6 0.03 0.03 -0.19 -0.3 0 -0.1 -0.1 -0.12 -0.13 -0.17 0.03 1.37 1.37 0.62];
x4 = [0 -1.24 -1.31 -1.31 -1.43 -1.63 -1.54 -3.82 -2.37 -2.37 -1.71 -2.78 -1.24 -1.31 -1.31 -1.43 -1.63 -1.54 -2.37 -0.55 -0.55 -0.61];
x5 = [0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 0.6 1.09 1.09 1.09 1.09 1.09 1.09 1.09 0.49 0.49 0.49];
x6 = [-3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 -3.82 0 0 0];
x7 = [2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 2.85 1.05 1.05 1.05];
x8 = [-2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -3.82 -3.82 -3.82];
X = [x1;x2;x3;x4;x5;x6;x7;x8];
y = [0.35 2 4.9 1.7 20 70 600 2 70 90 1.2 1.2 20 55 22 170 750 6500 720 24 6.6 7];
yy = log(y);

x = X;
t = yy;

% Choose a Training Function
% For a list of all training functions type: help nntrain
% 'trainlm' is usually fastest.
```

```
% 'trainbr' takes longer but may be better for challenging problems.
% 'trainscg' uses less memory. Suitable in low memory situations.
trainFcn = 'trainlm';  % Levenberg-Marquardt backpropagation.

% Create a Fitting Network
hiddenLayerSize = 8;
% net = fitnet(hiddenLayerSize,trainFcn);
net = feedforwardnet(hiddenLayerSize, trainFcn);

% Setup Division of Data for Training, Validation, Testing
net.divideParam.trainRatio = 70/100;
net.divideParam.valRatio = 15/100;
net.divideParam.testRatio = 15/100;

% Train the Network
[net,tr] = train(net,x,t);

% Test the Network
y = net(x);
e = gsubtract(t,y);
performance = perform(net,t,y);

% View the Network
% view(net)
% plotregression(t,y);

% Plots
% Uncomment these lines to enable various plots.
%figure, plotperform(tr)
%figure, plottrainstate(tr)
%figure, ploterrhist(e)
%figure, plotregression(t,y)
%figure, plotfit(net,x,t)

genFunction(net, 'netFcn');
y2 = netFcn(x);

net.userdata.note;
net.outputs;

test = [-0.1 0.6 0.6 -0.1 -0.1 0 0 0;
        -1.31 -3.82 -3.82 -1.31 -1.31 -1.24 -1.24 -1.24;
        -0.1 0.49 0.49 -0.1 -0.1 0 0 0;
        -1.31 0 0 -1.31 -1.31 -1.24 -1.24 -1.24;
        0.6 0 0 0 0 0 0 0.6;
        -3.82 -1.24 -1.24 -1.24 -1.24 -1.24 -1.24 -3.82;
```

```
        2.85 0 2.85 2.85 0 0 2.85 2.85;
        -2.4 -1.24 -2.4 -2.4 -1.24 -1.24 -2.4 -2.4];
test2 = [-0.1 0 -0.1 -0.12 -0.12 -0.1 -0.1 -0.1 -0.1;
         -1.31 -1.24 -1.31 -1.43 -1.43 -1.31 -1.31 -1.31 -1.31;
         -0.1 0 -0.1 -0.12 -0.12 -0.1 -0.1 -0.1 -0.1;
         -1.31 -1.24 -1.31 -1.43 -1.43 -1.31 -1.31 -1.31 -1.31;
         0.6 0.6 2.85 2.85 0 0 1.1 2.01 0;
         -3.82 -3.82 -2.4 -2.4 -1.24 -1.24 -1.32 -1.44 -1.24;
         2.85 2.85 2.85 2.85 2.85 2.85 1.1 2.01 0;
         -2.4 -2.4 -2.4 -2.4 -2.4 -2.4 -1.32 -1.44 -1.24];
testX1 = [0.49 0.49 0.49 0.49 0.49  0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0   0   0   0   0   0   0   0   0
0   0   0   1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0   0   0   0   0   0   0   0   0   0   0   0
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0   0   0   0   0   0   0   0   0   0   0   0   0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    -0.1    -0.1    -0.1    -0.1    -0.1    -0.1    -0.1    -0.1
-0.1    -0.1    -0.1    -0.1    0   0   0   0   0   0   0   0   0   0   0   0   0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49    0.49
0.49    0.49    0.49];
testX2 = [0 0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   -1.24   -1.24
-1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.71   -1.71   -1.71   -1.71
-1.71   -1.71   -1.71   -1.71   -1.71   -1.71   -1.71   -1.71   0   0   0   0   0   0   0   0   0   0   0   0   0
0   0   0   0   0   0   0   0   0   0   0   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24
-1.24   -1.24   -1.24   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
0   0   0   0   0   0   0   0   0   0   0   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24
-1.24   -1.24   -1.24   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
0   0   0   0   0   0   0   0   0   0   0   -1.31   -1.31   -1.31   -1.31   -1.31   -1.31   -1.31   -1.31   -1.31
-1.31   -1.31   -1.31   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24   -1.24
-1.24   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
0   0   0   0   0   0   0];
testX3 = [0 0   0   0   0   0   0   0   0   0   0   0   -0.1    -0.1    -0.1    -0.1    -0.1    -0.1    -0.1    -0.1
-0.1    -0.1    -0.1    -0.1    0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0   0
0   1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.16    1.77    1.77
1.77    1.77    1.77    1.77    1.77    1.77    1.77    1.77    1.77    1.77    -0.1    -0.1    -0.1    -0.1    -
0.1    -0.1    -0.1    -0.1    -0.1    -0.1    -0.1    -0.1    -0.19   -0.19   -0.19   -0.19   -0.19   -0.19   -
0.19   -0.19   -0.19   -0.19   -0.19   -0.19   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12
-0.12   -0.12   -0.12   -0.12   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13
-0.13   -0.13   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12   -0.12
-0.21   -0.21   -0.21   -0.21   -0.21   -0.21   -0.21   -0.21   -0.21   -0.21   -0.21   -0.21   -0.13   -0.13
-0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.13   -0.3    -0.3    -0.3    -0.3    -
```

```
0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-
0.1	-0.1	-0.1	-0.1	-0.1	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01	2.01	
2.01	2.01	2.01	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.39	0.39	0.39	0.39	0.39	
0.39	0.39	0.39	0.39	0.39	0.39	0.39	0.92	0.92	0.92	0.92	0.92	0.92	0.92	
0.92	0.92	0.92	0.92	0.92];
testX4 = [-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-
1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.24	-1.24	
-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	-1.24	1.24	1.24	1.24	1.24	
1.24	1.24	1.24	1.24	1.24	1.24	1.24	1.24	-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	
-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	-0.55	-0.55	-0.55	-0.55	-0.55	-0.55	-0.55	-0.55	
-0.55	-0.55	-0.55	-0.55	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	
-1.31	-1.31	-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	-1.71	
-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.63	-1.63	
-1.63	-1.63	-1.63	-1.63	-1.63	-1.63	-1.63	-1.63	-1.63	-1.63	-1.43	-1.43	-1.43	-1.43	
-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-1.43	-2.37	-2.37	-2.37	-2.37	-2.37	-2.37	
-2.37	-2.37	-2.37	-2.37	-2.37	-2.37	-2.17	-2.17	-2.17	-2.17	-2.17	-2.17	-2.17	-2.17	
-2.17	-2.17	-2.17	-2.17	-2.78	-2.78	-2.78	-2.78	-2.78	-2.78	-2.78	-2.78	-2.78	-2.78	
-2.78	-2.78	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	
-1.44	-1.44	-1.44	-1.44	-1.44	-1.44	-1.44	-1.44	-1.44	-1.44	-1.44	-1.44	-1.32	-1.32	
-1.32	-1.32	-1.32	-1.32	-1.32	-1.32	-1.32	-1.32	-1.32	-1.32	-1.31	-1.31	-1.31	-1.31	
-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-1.31	-2.36	-2.36	-2.36	-2.36	-2.36	-2.36	
-2.36	-2.36	-2.36	-2.36	-2.36	-2.36];
testX5 = [2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	
0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	
0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	
2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	
2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	
0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	
0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	
2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	
2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	
0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	
0	0	0	0.6	0.6	0.6	2.85	2.85	2.85	2.01	1.1	0	0	0	0	0.6	0.6	0.6	2.85	2.85];
testX6 = [-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	
-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	
-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-1.24	-1.24	
-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	
-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	
-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-
2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-
1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-
1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-
1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-
3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-
3.82	-2.4	-2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-
2.4	-2.4	-1.44	-1.32	-1.24	-1.24	-1.24	-1.24	-3.82	-3.82	-3.82	-2.4	-2.4	-2.4	-
```

```
1.44   -1.32   -1.24   -1.24   -1.24   -1.24   -3.82   -3.82   -3.82   -2.4    -2.4    -2.4    -1.44   -1.32   -
1.24   -1.24   -1.24   -1.24   -3.82   -3.82   -3.82   -2.4    -2.4    -2.4    -1.44   -1.32   -1.24   -1.24   -
1.24   -1.24   -3.82   -3.82   -3.82   -2.4    -2.4    -2.4    -1.44   -1.32   -1.24   -1.24   -1.24   -1.24   -
3.82   -3.82   -3.82   -2.4    -2.4];
testX7 = [2.85  2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0
2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85
2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16
2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85
2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1
1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01
1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1
2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77
1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0
2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85
2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16
2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85
2.01    1.1 2.85    2.01    1.1 1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1
1.77    1.16    2.85    2.01    1.1 0   2.85    2.01    1.1 2.85    2.01    1.1 1.77    1.16];
testX8 = [-2.4  -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4
-1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32
-1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -
1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -
2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -
1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -
1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -
1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -
1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -
1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -
2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -
1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -
1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -
1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -
1.24   -2.4    -1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -
1.44   -1.32   -2.4    -1.44   -1.32   -0.55   -1.71   -2.4    -1.44   -1.32   -1.24   -2.4    -1.44   -1.32   -
2.4    -1.44   -1.32   -0.55   -1.71];
test3 = [testX1;testX2;testX3;testX4;testX5;testX6;testX7;testX8];

testAns_inLog = netFcn(test);
testAns = exp(testAns_inLog);
testAns_inLog2 = netFcn(test2);
testAns2 = exp(testAns_inLog2);
testAns_inLog3 = netFcn(test3);
testAns3 = exp(testAns_inLog3);
```

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