Chapter 2
Crystal Growth

2.1 Introduction

During the latter half of the 19th century, the study of matter in the nearly perfect molecular disorder of the gaseous state led to the kinetic theory and thermodynamic concepts that prominently shaped progress in chemistry and physics into the next century. Since its inauguration, the National Bureau of Standards (NBS) contributed to that progress by its careful critical measurements at the highest attainable sensitivity, as is well documented in Refs. [1][2]. In the 20th century, the study of the nearly perfect molecular order of the solid state and its interactions with photons—that is the study of crystallography—has prominently shaped spectacular further progress in physics and chemistry. Crystallography today is at the center of all materials science and engineering, including solid-state physics, geology, metallurgy, ceramics, biophysics, and biochemistry. Thus crystallography has become a prominent key to a widening scientific understanding of our material universe, and even the life within it. NBS, now renamed the National Institute of Standards and Technology, has again contributed by its predilection to careful experimentation and critical measurements at the highest attainable sensitivity. In choosing my illustrative examples of NBS/NIST achievements in crystallography,.

2.2 Crystallization

The theory of atomic scale order in crystals had long been established based on morphological and optical studies. This order
could not be directly observed in the 19th century. Besides, many solids do not exhibit long-range order; they are not crystalline, but amorphous. Many crystals were long known to shatter at characteristic temperatures when cooled below their melting points. Melt growth, especially of metal crystals, had been extensively studied. Vapor growth had been observed, such as in ice crystals, since the spealinr. Solution growth of crystals had been most widely studied, variabilities of their solubilities carefully measured, and the growth of macroscopic crystals had been demonstrated for many substances. The resistance to being crystallized, particularly of certain sugars, was known when the problem of reliable cane sugar assay was brought to the NBS in the face of controversy between suppliers, refiners, and distributors. The Federal Government was involved by virtue of its import duties on sugar. Frederick Bates and his colleagues [3] transformed the industry, not only by perfecting the optical measuring instrument, the saccharimeter, but equally by the publication of credible measurement protocols. Expanding upon this work in typical NBS fashion, its chemical laboratory became a prominent center in the world of basic sugar chemistry that revealed fascinating details of molecular ring formulae and optically active crystal structures. This NBS work is documented, for instance, in Ref. [4].

2.3 Purification by Crystallization

It had also long been known in science and exploited by the manufacturing industry that many substances can be successfully purified from contamination by crystallization from melt and from solution. Chemists knew how to exploit the phase rule, a widely applicable development from the study of gases. They also observed
that large crystals tend to be purer than small crystals of the same substance because the latter have larger ratios of surface area to crystal volume. Impurities are preferentially held at crystal grain boundaries. The selectivity of the growing crystal for incorporating molecules of only a specific type and chirality in sugars was found at NBS to depend not only on crystal phase, but also on crystal habit and temperature [4,5]. Before the implications of dislocations had been widely understood, Charles Saylor at NBS stood out among his colleagues with a deep understanding of the processes of purification by crystallization. In Ref. [6] he refined the method of microscopic measurement of refractive index by immersion practiced by mineralogists generally and currently in a critical, NIST-advocated technique for distinguishing asbestos minerals. Saylor’s group understood well how to combine crystal density with optical and chemical properties to assess the purity of crystals [7]. John Torgesen, supported by his technician, Avery Horton, was widely regarded at NBS as the most successful experimenter in crystal growth. His work is exemplified by his large ammonium dihydrogen phosphate crystals and their habit modifications by ion additions, as well as by his purification of “ultrapure” reagent-grade benzene by melt recrystallization. He has left few direct traces of his influence in the literature except for two items, one on crystallography in chemical research [8], and another on a potential manufacturing application [9]. Torgesen’s expertise, however, was an important pillar in the creation of the International Conference on Crystal Growth, of its equivalent and active American Association for Crystal Growth, and, later, of the corresponding International Journal for Crystal Growth (North Holland). Starting with a Conference at Harvard University [10], many of these organizations have ever since been major vehicles for disseminating the rapidly expanding science
and technology of crystal growth. So numerous were the NBS contributions to such investigations that, in 1962, C. F. Yost of the Advanced Research Projects Agency (ARPA) of the U.S. Department of Defense agreed with I. C. Schoonover of NBS to fund jointly a 3 year program of unclassified research at NBS on crystal growth and characterization. At that time it had become clear that progress in science and technology often depended on breaking down barriers to cooperation between specialists in different disciplines or organizational divisions. Thus, Schoonover was anxious to experiment with “matrix management” across lines of organizational responsibilities without loss of the established NBS management structure. ARPA agreed to give the NBS program manager complete freedom of choice of tasks; while Schoonover gave instructions for many innovative tasks to be so supported, each with very little “seed” money. An important selection criterion was that each task had to be strongly supported also within the division from which it was proposed. In the event, in excess of a hundred separate tasks were so funded from 11—that is most—NBS research divisions. It is clearly impossible to describe here the individual summaries given in Refs. [11–14]. By a glance at this record one cannot but notice how many of these studies continued self-supported by divisions long beyond the time limit of this ARPA program and extended into contributions mentioned in Refs. [1] and [2] or in other papers in this Special Issue. They were intertwined with core research activities of very many groups at NBS that did not describe crystallography as their primary purpose. Yet, their favored research dealt with some of the basic problems of growing and characterizing crystals. From among the many ARPA studies, let me first single out research by Hans Frederikse’s group on semiconductors based on d-electrons (as opposed to the more usual
They investigated the band structure of reduced strontium titanate (0.1 % to 0.01 % oxygen deficiency). It is cubic (perovskite structure) down to liquid helium temperatures. From knowledge of the density of states [15] and calculations of the energy band structure [16], they were able to prove theoretically and to confirm experimentally that this semiconductor becomes a superconductor, albeit at only 0.3 K, too low for this specific compound to have practical applications.

2.4 The Perfection of Crystals

Physical properties of crystals can be measured for characterizing the chemical and physical perfection of crystals. Among these properties the most important has probably been that of density. Its impact is described in Ref. [1] (see p. 193ff), but there the subjects are so condensed that it seems appropriate to emphasize here the cardinal role played by density standards and measuring methods developed at NBS. Combined with relative atomic-mass measurements they led directly to what remains one of the principal routes to the interconnected fundamental constants of physics. For the past 40 years, NBS/NIST has excelled in isotopic composition measurements which, with the highly accurately known isotope mass values, lead to the mean relative atomic mass values of polynuclidic elements in their characteristic terrestrial compositions. X-ray spacings in crystals, another great NBS specialty, and density of crystals of known chemical and isotopic composition yield the Avogadro constant by the XRCD (X-Ray Crystal Density) method. Its latest international evaluation has recently been published [17]. For stoichiometrically well characterized crystals the mean atomic or molecular mass values could be determined from the density and
crystal cell volume alone without measuring isotopic composition [18]. In practice, however, to this date very few crystals have been of adequate physical and chemical perfection for this method to impact current knowledge embedded in the biennially revised tables of the relative atomic mass values of the elements [19]. Uniquely pure and dislocation-free silicon crystals are important exceptions that derive from the intense interest of the electronic industry. These crystals have been used for the previously mentioned measurement of the mean atomic mass of natural silicon and the Avogadro constant [17]. Earlier work on crystal perfection had to rely on external habit, some optical properties, and angular broadening of x-ray diffraction maxima. The last of these methods was exploited successfully at NBS especially in work on cements and fiber-forming polymers as described in other articles of this series, as seen also from Refs. [11–14]. The almost universal substructure of most crystals is characterized by mosaics, with slight relative misalignment. It permits the interpretation of diffraction intensities, by use of the kinematic theory, in terms of ionic, atomic, and molecular structure. During most of the century, this was by far the most important output of crystallographic studies. Those aspects, however, are not covered in this article, but NBS contributions on this topic are well represented elsewhere in this Special Issue. In previously quoted Refs. [11–14] the interest in Laue’s original dynamical theory of x-ray diffraction came back into prominence, first by methods of x-ray imaging and also by exploiting anomalous x-ray transmission by highly perfect crystals. Deslattes and colleagues at NBS succeeded in simultaneously comparing x-ray transmission spacing periods with light interferometry on crystals moved smoothly on an atomic scale [1]. Equivalent procedures were used in the x-ray spacing
measurements for silicon crystals for the XRCD method deriving the Avogadro constant [17].

2.5 Crystal Growth Technique

Metal-Organic Frameworks are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. In some cases, the pores are stable to elimination of the guest molecules (often solvents) and can be used for the storage of gases such as hydrogen and carbon dioxide. Other possible applications of MOFs are gas purification, gas separation, catalysis and sensors. A metal-organic framework (MOF) is composed of two major components: a metal ion or cluster of metal ions and an organic molecule called a linker. The organic units are typically mono-, di-, tri-, or tetravalent ligands.[20] The choice of metal and linker has significant affects on the structure and properties of the MOF. For example, the metal's coordination preference influences the size and shape of pores by dictating how many ligands can bind to the metal and in which orientation.

There is no consensus in the scientific literature about the definitions of the terms coordination polymer and metal-organic framework. Some authors suggests definitions based on chemical bonding[21] others propose that the terms coordination polymer and metal-organic framework are synonyms[22]. An IUPAC project was initiated in 2009 to address the terminology issues in this area and will deliver its final report in 2011[23,24].
<table>
<thead>
<tr>
<th>Dimensionality of Inorganic</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<td>Hybrid Inorganic Layers</td>
<td>3-D Inorganic Hybrids</td>
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<td>Mixed Inorganic-Organic Layers</td>
<td>Mixed Inorganic-Organic 3-D Framework</td>
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<tr>
<td>3</td>
<td>3-D Coordination Polymers</td>
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</table>

**Secondary building units**

Describing and organizing the complex structures of MOFs could be a difficult and confusing task without a logical, unambiguous set of classifications. Recently, a system of nomenclature has been developed to fill this need. Inorganic sections of a MOF, called secondary building units (SBU), can be described by topologies common to several structures. Each topology, also called a net, is assigned a symbol, consisting of three lower-case letters in bold. MOF-5, for example, has a **pcu** net. The database of net structures can be found at the Reticular Chemistry Structure Resource[21].
# Common ligands in MOFs

<table>
<thead>
<tr>
<th>Common name</th>
<th>IUPAC name</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid</td>
<td>ethanedioic acid</td>
<td>HOOC-COOH</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>propanedioic acid</td>
<td>HOOC-(CH₂)-COOH</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>butanedioic acid</td>
<td>HOOC-(CH₂)₂-COOH</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>pentanedioic acid</td>
<td>HOOC-(CH₂)₃-COOH</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>benzene-1,2-dicarboxylic acid</td>
<td>C₆H₄(COOH)₂</td>
</tr>
<tr>
<td></td>
<td>o-phthalic acid</td>
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<tr>
<td>Isophthalic acid</td>
<td>benzene-1,3-dicarboxylic acid</td>
<td>C₆H₄(COOH)₂</td>
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<td></td>
<td>m-phthalic acid</td>
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</tr>
<tr>
<td>Terephthalic acid</td>
<td>benzene-1,4-dicarboxylic acid</td>
<td>C₆H₄(COOH)₂</td>
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<tr>
<td></td>
<td>p-phthalic acid</td>
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<tr>
<td>Citric Acid</td>
<td>2-Hydroxy-1,2,3-propanetricarboxylic acid</td>
<td>(HOOC)CH₂C(OH)(COOH)CH₂(COOH)</td>
</tr>
<tr>
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<td>benzene-1,3,5-tricarboxylic acid</td>
<td>C₉H₆O₆</td>
</tr>
<tr>
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<td>1H-1,2,3-triazole</td>
<td>C₂H₃N₃</td>
</tr>
<tr>
<td>pyrotriazole</td>
<td>1H-1,2,4-triazole</td>
<td>C₂H₃N₃</td>
</tr>
<tr>
<td>Squaric acid</td>
<td>3,4-Dihydroxy-3-cyclobutene-1,2-dione</td>
<td>C₄H₂O₄</td>
</tr>
</tbody>
</table>
Synthesis of MOFs

The study of MOFs developed from the study of zeolites, with very little change in synthetic technique. MOFs and zeolites alike are produced almost exclusively by hydrothermal or solvothermal techniques, where crystals are slowly grown from a hot solution of metal precursor, such as metal nitrates, and bridging ligands[26]. Zeolite synthesis often makes use of a variety of templates, or structure-directing compounds, and a few examples of templating, particularly by organic anions, are seen in the MOF literature as well[27,28]. A particular templating approach that is useful for MOFs intended for gas storage is the use of metal-binding solvents such as N,N-diethylformamide and water. In these cases, metal sites are exposed when the solvent is fully evacuated, allowing hydrogen to bind at these sites[29]. Post-synthetic modification of MOFs opens up another dimension of structural possibilities that might not be achieved by conventional synthesis. A great deal of recent work explores covalent modification of the bridging ligands[30]. Of particular interest to MOFs for hydrogen storage are modifications which expose metal sites. This has been demonstrated with post-synthetic coordination of additional metal ions to sites on the bridging ligands[29,30], and addition and removal of metal atoms to the metal site[29,31]. Since ligands in MOFs typically bind reversibly, the slow growth of crystals allows defects to be redissolved, resulting in a material with millimeter-scale crystals and a near-equilibrium defect density. Solvothermal synthesis is useful for growing crystals suitable to structure determination, because crystals grow over the course of hours to days. However, the use of MOFs as storage materials for consumer products demands an immense scale-up of their synthesis. Scale-up of MOFs has not been widely studied, though several groups have demonstrated that microwaves can be used to
nucleate MOF crystals rapidly from solution[32,33]. This technique, termed "microwave-assisted solvothermal synthesis", is widely used in the zeolite literature[26], and produces micron-scale crystals in a matter of seconds to minutes[32,33], in yields similar to the slow growth methods. A solvent-free synthesis of a range of crystalline MOFs have been described by Stuart James and his group[34]. Usually the metal acetate is reacted with the organic ligand of choice, placed in a stainless steel vessel with a ball bearing, mixed and grinded in a ball mill mixer. Cu$_3$(BTC)$_2$ has been synthesised in this way with a quantitative yield. The reaction is quick and can be monitored with XRPD. In the ball mill it is found that the morphology of the MOF may differ from the expected. In the case of Cu$_3$(BTC)$_2$ the morphology of the solvent free synthesised product was the same as the industrial made, Basolite C300. It is thought that localised melting when the molecules collide may assist the reaction. The formation of acetic acid as a by-product in the reactions in the ball mill may also help in the reaction having a solvent effect[35] in the ball mill.

**Composite MOF materials**

Another approach to increasing adsorption in MOFs is to alter the system in such a way that chemisorption becomes possible. This has been achieved by making a composite material, which contains a MOF and a complex of platinum with activated carbon. In an effect known as hydrogen spillover, H$_2$ can bind to the platinum surface through a dissociative mechanism which cleaves the hydrogen molecule into two hydrogen atoms and enables them to travel down the activated carbon onto the surface of the MOF. This produced a three-fold increase in the room-temperature storage capacity of a MOF; however, desorption can take upwards of 12 hours, and
reversible desorption is sometimes observed for only two cycles [36,37]. The relationship between hydrogen spillover and hydrogen storage properties in MOFs is not well understood, but further research in this direction may provide inexpensive boosts in hydrogen storage capacity.

**Instrumentation and Theory**

Distillation separates chemicals by the difference in how easily they vaporize. The two major types of classical distillation include continuous distillation and batch distillation. Continuous distillation, as the name says, continuously takes a feed and separates it into two or more products. Batch distillation takes on lot (or batch) at a time of feed and splits it into products by selectively removing the more volatile fractions over time.

**Rotary Evaporation**

In both traditional chemistry labs and our crystal develop technology lab, the rotary evaporator, or rotovap, is an instrument used to distill a solvent and produce crystals in the form of MOF. (Everyone calls it a “rotovap” even though rotovap is a brand name). The purpose of distillation is to separate a given mixture into its components based on their respective volatilities, through the process of evaporation and condensation (liquid-gas-liquid). We use the rotovap for two main purposes: 1) to concentrate non-volatile components in a mixture (for example, concentrating the purest and freshest flavors from a blood orange by removing the water), and 2) to extract the volatile aroma and flavor molecules from mixtures gently and at low temperatures. The key to understanding any distillation is to remember that it is a separation. Sugars, acids, colors, and most bitter compounds are separated from aromas, alcohols, water, and
small flavor molecules, etc. What is phenomenal about rotovap distillation, as opposed to standard distillation, is that it can separate food compounds from one another without altering them.

Two key components of the rotovap allow for a gentle, precise, and efficient distillation not found in conventional distilling apparatuses: 1) the solvent is removed under vacuum, which lowers its boiling point and send back to reaction, eliminating the need for high-temperature distillation, and 2) the rotation of the evaporating flask, immersed in a heated water bath, increases the surface area of the product, greatly speeding distillation and also, through forced convection, keeping the mixture evenly mixed and heated to promote stable, even evaporation. An additional benefit of laboratory-type stills over Uncle Jesse moonshine-type pot stills is that laboratory condensers, being sealed and made of glass, are easy to visually monitor and adjust. We can, therefore, recover almost 100% of the solvent. While scientists are almost solely concerned with the residue left over after the solvent has evaporated, we are proud members of the minority interested in the distillate itself. What they call a solvent, we call flavor. To this end, we have redesigned a mid 1980’s vintage Buchi Rotovap EL-130 and tailored it to our culinary endeavors. Therefore, beware! The primer that follows is not a standard rotovap primer. It is a primer for those individuals interested in distilling not petrochemicals, but gin. And it’s not a primer on standard distillation, which is usually concerned with maximizing the purity of the distillate. We want to maximize the impurity. But we get ahead of ourselves. Let’s start with an overview of the distillation process.
Here is the basic rotary evaporator setup. We'll go into greater detail on some of these parts in next section.

![Rotary Evaporator Setup](image1)

**Figure 2.1: Rotary evaporator setup**

![Rotary Evaporator Working](image2)

**Figure 2.2: Working of Rotary evaporator setup**
Details of Parts

Before getting into greater detail on the rotovap process, it is important to understand the theory behind the instrument. Four components affect the rate of distillation:

1. **Temperature of the Heating Bath:**

   The higher the temperature of the bath, the faster your product will boil at a given pressure. The boiling temperature of your product is determined by the pressure of the system. A higher water bath temperature will not raise the temperature of your product above boiling, but it will put in energy faster. In standard distillation, the pressure is kept constant and the temperature of the product slowly rises with time as more and more product boils off; the rate of distillation is determined by heat input. In a rotovap, the temperature of the heat input (and, roughly, the temperature of the product) is kept constant and the distillation is adjusted by controlling the pressure.

2. **Pressure of the Distillation:**

   The lower the pressure, the lower the boiling point of your product and the faster you will distill at a given bath temperature (i.e., at a given heat input).

3. **Speed of Rotation and Size of the Flask:**

   Generally, the larger the flask and the higher its RPM, the quicker the evaporating process (there is more new surface area exposed per unit time).
4. Size and Power of the System:

The speed of distillation in a given system is limited primarily by the condenser’s ability to condense the solvent vapor (it is rare to be limited by the heater). If you allow too much vapor to rush into the condenser, it will overload and be unable to work efficiently, which will result in a loss of valuable volatiles. According to the manufacturer Buchi, to avoid saturation, you should monitor the pressure of the system such that 2/3 of the condenser is consistently covered with condensate. If liquid begins to form on the top 1/3 of the coil, the incoming vapor runs the risk of being sucked out into the vacuum pump and being lost forever. In practice we often let the condensation get closer to 3/4 of the way up the condenser. Another indicator is the “condensation line,” usually above the area where you see actual liquid on the coils. This is easy to see in water distillations, but hard to see in alcohol distillations. Unfortunately, it takes a while to become comfortable adjusting the pressure. Until then, your “get out of jail free card” is the “air button.” A quick push of this button will raise the system pressure, clearing the condenser and allowing you to start afresh. The speed of distillation is important because the faster you distill without saturating, the better the product. This is a fact.

Rotovap Structure and Design

Now we’ll revisit some key components of the rotovap, providing more details on setup.

**Evaporation Flask:** The mixture to be evaporated starts in this flask, which rotates in a heated water bath. The size of your flask determines how much liquid you can distill at one time. Bigger is
better, so long as your condenser can handle it. Ours is 250 ml. Ideally, we want to attach the flask to the rotovap first, and then pump the solvent directly in. Don’t fill the flask more than half full or you’ll have problems with boil-over. And you’ll decrease surface area and slow down distillation. Our flask has a special wide neck, which makes it easy to get product in and out. If your machine can’t accommodate a 250 ml flask, invest in an evaporation beaker, a wide mouth beaker that can be hooked up to a rotovap.

**Rotary Drive:** Controls the rpm of the flask. We keep ours at around 120.

**Water Bath:** Filled just up to the point where the mixture in the flask is submerged, the water bath transfers heat to the mixture quickly and efficiently. Water is the optimal medium to use since it’s safe and cheap, distributes heat well, and has a high specific thermal capacity (though on certain occasions, it may be necessary to heat the mixture using an oil bath).

**Vapor Duct:** This is where the vapor is transmitted from the evaporation flask to the condenser. It is also where your system is most likely to leak. Make sure your vapor duct is super-duper clean and properly centered. On our EL model, the vapor duct is stationary, and the seal rotates around it, as opposed to most other models, where the seal is stationary and the vapor duct rotates. This difference won’t make matter to most people, but since the EL series aren’t made anymore, they are often cheaper. They also allow reflux distillation (for the hard core rotovap users out there), but the seal goes bad on them more often.
**Rotary Vacuum Seal:** These cost 50 bucks a pop for a tiny ring of rubber so take good care of them! Remove the seal from the rotovap when you’re not running it. The manufacturer says to never grease them because grit can get into the grease and ruin the vapor duct. We do anyway because is the only way we can get the seal to work. Make sure you install them the right way (check your manual for details).

**Condenser:** As solvent surrounds the condensing coil with vapor, this part of the instrument turns the vapor back into a liquid (using the same amount of energy to cool that was originally needed to heat the liquid into a vapor). The vapors condense into liquid droplets that, by the power of gravity, make their way down the coil into a receiving flask.

You need enough cooling power in the condenser to condense everything that has vaporized in the evaporation flask, or the condenser will get saturated. This will contaminate your pump and make the mixture lose flavor. The more cooling power your condenser has, the more liters per hour you can distill without saturating and without losing temperature. There is no point, however, in having more cooling capacity than you have heating capacity in the water bath.

Another type of condenser is the “cold finger,” which consists of a sleeve filled with extremely cold liquid, like liquid nitrogen or dry ice and acetone, instead of a coil. Cold finger condensers completely freeze the distillate. They get extremely good capture of the volatile aromas, but I don’t like them because you have to thaw them out
between batches. And there is no way to tell when you are done because you can’t taste the product as you go (more on that later).

**Vacuum Pump/Controller:** The rotovap would be just a souped-up still if it weren’t for the vacuum pump. The vacuum is what lowers the boiling point of product and allows us to do distillations all the way down to room temperature or below.

Choosing a good pump is important. First, your pump needs to be powerful enough to obtain a reasonable vacuum in a reasonable amount of time. Second, your pump needs to be able to reach an ultimate vacuum (the highest level your machine has the ability to achieve) good enough for the work you are doing. Atmospheric pressure is about 1000 millibar. To do straight liquor work at 60°C, your pump needs to be able to go down to 40 millibar without breaking a sweat. To do all liquor work down to 40°C your pump better be able to pull an ultimate vacuum of 20 millibar. To do syrups or for water-based work, your pump better get down to 8-10 millibar. Most people fail by getting a pump with an inadequate ultimate vacuum.

Water aspirators will not work for low temperature distillation; they also have low flow rates. I have tried using them with ice water, in big banks, etc. I don’t like them. Refrigeration vacuum pumps work well and are cheap, but are difficult to control, noisy, and fill the air with an oil-haze. They need oil to operate and don’t come with a filter, like the pumps in a vacuum sealer. If you do decide to use one, leave a rag over the outlet to catch oil. Also never, ever turn off the pump when under vacuum or you risk sucking oil back into your system. First vent the system, and then turn off the pump. To control a
refrigeration pump, you need to install a bleeder needle valve between the pump and the rotovap. Let the pump run and adjust the vacuum level using the valve. Also install a second air/vent valve, preferably push-button. This is your emergency button that quickly lets air into the system to stop a boil-over. Other than noise, oil-haze, and control difficulties, the other problem with oil-based pumps is that the oil gets contaminated whenever you saturate the condenser.

**Product In/Air Vent Valve:** This valve, when turned down, uses the vacuum in the system to suck product into the evaporation flask without breaking the vacuum. It’s very handy. The internal tube is quite small so don’t try to suck anything through it that hasn’t been strained. Turn the valve in the other direction to let air into the system. When we are starting we can use this as our “emergency button,” but it is not recommend. It’s not fast enough and requires that we reach up and twist it, as opposed to the air valve attached to the vacuum pump.

**Receiving Flask:** This is where the distillate goes. It’s the solvent killer, the Achilles heel of the standard rotovap. The distillate tends to redistill into the condenser and then back down again into the flask. Each time this happens a little solvent gets lost out the top of the condenser (we don’t re-condense 100%). As the result averages out to whatever the main solvent is (usually alcohol and water). This isn’t a problem for scientists, who only dealing with one or two solvents. But for us, the “solvent” is the aroma compounds! There can be dozens of these compounds in a single distillation. Some are only present in tiny quantities but are key to the final product. To improve our results, chill the receiving flask and remove it often to dump out the distillate. To really solve the problem, read on.
2.6 Material and Method

[1] Materials

The ligand which is a Schiff base obtained from Salicyldehyde and Ethelenediamine were used. The stock solution of NiCl₂, and CuCl₂ were prepared.

[2] Preparation of Schiff base

Salicyldehyde (1.4919 gm 0.1 mol) solution in ethanol and Ethelenediamine (1.0814 gm 0.1 mol) solution in hot water were taken in round bottomed flask, 50 ml absolute ethanol was added and the mixture was refluxed for 3 hour. The refluxed mixture was put in ice bath, then orange coloured precipitate was obtained. It was suctioned filtered and washed with distilled water. Schiff base obtained was dried and kept in vacuum dessicator. The pure Schiff base was recrystallized from absolute ethanol.

[3] Preparation of Crystals

The crystals were prepared by mixing Schiff base (0.1mol) in hot ethanol solution to (0.1mol) metal chloride salt solution prepared in distilled water. The schiff base solution was added slowly with continuous stirring to metal solution. It was refluxed for 2 hours and after refluxation, the mixture was heated for 10 minutes till the contents was reduced to half. Then the metal crystals precipitated out after being cooled. The precipitate was filtered and washed with the distilled water. All complexes were dried and kept in vacuum dessicator.

2.7 Chemistry of Crystal growth

All chemicals used were of reagent grade. Their standard
solutions were prepared by using doubly distilled CO\(_2\) free water. Metal salt were standardized by complexometric EDTA titration method conductivity water is used throughout the experimental work. Digital µ 361 pH meter with readability + 0.001 with combined glass calomel electrode have been used for pH metric study. Stoichiometrically 1:1:1 concentration of M\(^1\), M\(^2\), L\(_1\) and L\(_2\) were maintained in the solution. Metal ligand mixtures of following compositions were prepared for titration keeping total volume 50ml in each case (µ=0.2 M NaClO\(_4\)). The concentration of ligand and metal solution were checked by pH metric titration against 0.2 N carbonate free sodium hydroxide solution.

The following sets were prepared for titration.

(A) Known amount of HClO\(_4\).

(B) Free HClO\(_4\) + known amount of ligand L\(_1\).

(C) Free HClO\(_4\) + known amount of ligand L\(_2\).

(D) Free HClO\(_4\) + known amount of ligand L\(_1\) + known amount of metal [M\(^1\)] (Binary).

(E) Free HClO\(_4\) + known amount of ligand L\(_2\) + known amount of metal [M\(^1\)] (Binary).

(F) Free HClO\(_4\) + known amount of ligand L\(_1\) + known amount of metal [M\(^2\)] (Binary).

(G) Free HClO\(_4\) + known amount of ligand L\(_2\) + known amount of metal [M\(^2\)] (Binary).

(H) Free HClO\(_4\) + known amount of ligand L\(_1\) + known amount of ligand L\(_2\) + known amount of metal [M\(^1\)] (Ternary).
(I) Free HClO$_4$ + known amount of ligand $L_1$ + known amount of ligand $L_2$ + known amount of metal [M$^2$] (Ternary).

(J) Free HClO$_4$ + known amount of ligand $L_1$ + known amount of ligand $L_2$ + known amount of metal [M$^1$] + known amount of metal [M$^2$] (Quaternary).

(i) $M^1L_1$ or $L_2$ and $M^2L_1$ or $L_2$ → 1:1 Binary mixtures.

(ii) $M^1L_1L_2$ and $M^2L_1L_2$ → 1:1:1 ternary mixtures.

where $M^1$, $M^2$ are Co$^{II}$, Ni$^{II}$, as required

$L_1$ = Salicyldehyde

$L_2$ = Ethelenediamine

Crystals of ternary mixtures $M^1L_1L_2$ and $M^2L_1L_2$ were used for further work.

2.8 System Used

Instrument Name: All glass double distillation unit, with borosilicate boiler, borosilicate condenser & Quartz Heater, Vertical type.
**Specification:**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dist. Water o/p capacity</td>
<td>1.5 lt/hr</td>
</tr>
<tr>
<td>Electrical requirement</td>
<td>230-250 volts</td>
</tr>
<tr>
<td></td>
<td>Single Phase 1.5x2 Kw</td>
</tr>
<tr>
<td></td>
<td>Quartz heater</td>
</tr>
<tr>
<td>Cooling water consumption</td>
<td>100 lt/hr</td>
</tr>
<tr>
<td>Biological Activity</td>
<td>Pyrogen free</td>
</tr>
<tr>
<td>pH</td>
<td>6.9 – 7</td>
</tr>
<tr>
<td>Conductivity S/cm</td>
<td>&lt; 1X 10^-6</td>
</tr>
<tr>
<td>Distillate Temp</td>
<td>65-75 °C</td>
</tr>
</tbody>
</table>

The boiler is made of high purity quartz and the condenser is of borosilicate/quartz material. The built in heater provides of minimum loss of heat and production of material. The unit is mounted on powder coated metal stand with electrical connections and is easy to dismantle and assemble the unit. Fiber glass insulated wire and silicon rubber boot resist high temperature.

**Spares for This Unit:**

1. Borosilicate boiler with water leveler 1.5 lt.
2. Condenser 1.5 lt.
3. Quartz new type heater B-34 complete unit.
4. Flasks – Boling, round bottom, short neck with interchangeable joint.
Capacity – 250 ml

Approx Height – 140 mm

All apparatus were used have high quality and Pore size of about 90 – 150 microns. All apparatus have excellent resistant to chemical attack. All apparatus are incorporating them are mainly design for the application of vacuum or for passage of gases at relatively low pressure. In all cases the differential pressure must not exceed 100 KN/m$^2$ (15 psi). All apparatus are particularly suited for drying to constant weight. All apparatus at room temperature can be placed directly 150 °C, although customary practice is to dry at 110 °C. It is advisable that rate of heating should not be more than 2 °C/min. This prevents internal strains caused by excessive temperature differences between the surrounding glass vessel and the sintered disk, which can lead to fracture of apparatus.

### 2.9 Crystals Specification

Photographs and Dimensions of all crystals were measured at Laljibhai Chaturbhai Institute of Technology (LCIT), Mehsana. All apparatus were used have high quality with 5 MP cameras.
Crystal of Cu(II) with Salicyldehyde and Ethelenediamine ligand

Figure 2.3 Photograph of crystal Cu(II) in single form

Size: 0.54 mm length and 0.48 mm width

Crystal of Ni(II) with Salicyldehyde and Ethelenediamine ligand

Figure 2.4 Photograph of crystal Ni(II) in single form

Size: 0.52 mm length and 0.31 mm width
References


3. Polarimetry (1914), NBS Circular 44.


35. Braga D. (2007), Cryst Eng Comm, 9, p879
