

READING SELECTION FOR STUDENTS OF CHEMICAL ENGINEERING

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This book covers different aspects about chemistry subject and other related ones. Our goal is to give to students elementary tools to use the English language in their specialty. Here, they can find different grammatical structures in the texts as well as an example of paper, and graphic that future chemical engineers need to know.

When you finish your course you should be able to:

1. Know some common technical words used in the chemical engineering work.
2. Answer comprehension questions about the reading.
3. Make an oral presentation about the main ideas of the text.
4. Translate into Spanish a text about chemical subjects.
5. Write an abstract in English.
6. Write an elementary report (paper).

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Note:

In the text you will find some dark words. They are technical words. You should learn them

CHAPTER I RESPIRATION:

We all need air. Air is a mixture of non-metallic elements and compounds of non-metallic elements. If we are deprived of it for more than a few minutes we become unconscious. This leads on to brain damage which may mean loss of speech, or paralysis, or even death. Our bodies need air, or more correctly, oxygen.

As we breathe in, air passes into the lungs through two large tubes called bronchi. These branch into many other small tubes called bronchioles. At the end of the bronchioles there are millions of tiny hollow bags called air sacs which are surrounded by blood vessels. (See figure 8.) The blood absorbs oxygen from the air sacs and this oxygen is then pumped by the organs of the body and the millions of cells that need it in order to function. In these cells, the oxygen reacts with compounds taken from the food we eat. These reactions produce energy, and carbon dioxide, which is carried by the blood back to the lungs, passed into the air sacs, and exhaled.

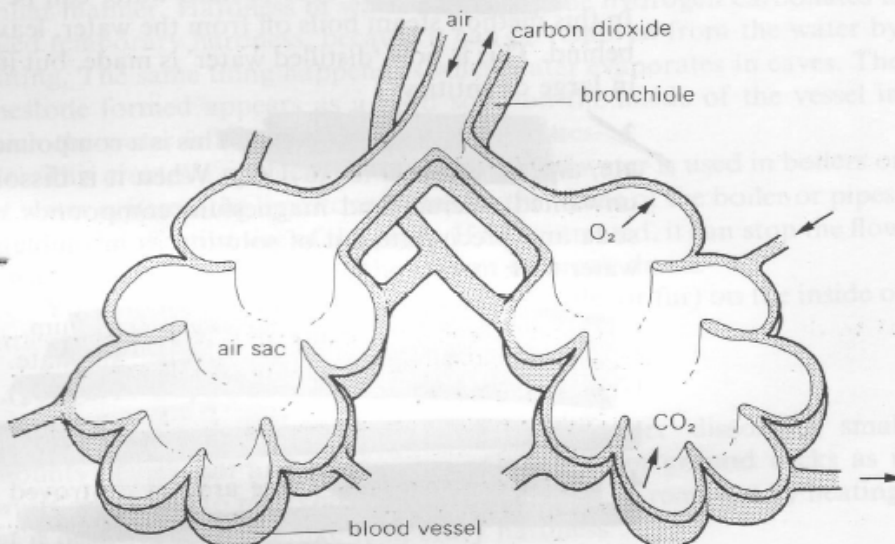
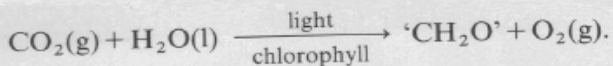


Figure 8

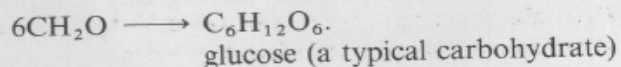
Air sacs in the lung.

All green plants absorb carbon dioxide through their leaves, and water through their roots. They then need sunlight as a source of energy, and the green pigment called *chlorophyll* as a catalyst. With raw materials, energy, and catalyst, they produce carbohydrates which are the main building blocks that they need. At the same time, they release oxygen, which is produced and not required.



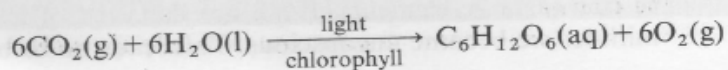
sugars

'CH₂O' is the building block for many different starches and (carbohydrates). For example:



es and

The process of turning carbon dioxide and water into carbohydrate oxygen is called *photosynthesis*.



ISOTOPES: DIFFERENT FORMS OF THE SAME ELEMENT.

Isotopes are different forms of the same element. They have the same number of protons and electrons but different numbers of neutrons. They have the same atomic number but different mass numbers.

If you look in the list of accurate masses you will see that the atomic mass of chlorine is given as 35.453. This is the relative atomic mass of chlorine and it is the average mass number of mixture of the two isotopes in naturally occurring chlorine. Naturally occurring chlorine contains 75 % of $^{35}_{17}\text{Cl}$, and 25 % of $^{37}_{17}\text{Cl}$. So you can see that the relative atomic mass is going to be much nearer 35 than 37.

The relative atomic mass for many of the elements is not a whole number. These elements consist of a mixture of naturally occurring isotopes.

For elements which are a mixture, we must always use the relative atomic mass. Mass numbers are only used for pure isotopes.

Another example of an element which has isotopes is hydrogen.

There are three isotopes of hydrogen:

^1_1H	^2_1H	^3_1H
protium	deuterium	tritium

You can see from the mass numbers that an atom of protium has no neutrons in its nucleus, deuterium has one neutron, and tritium has two neutrons. Each isotope has one proton and one electron. Naturally occurring hydrogen contains 99.985 % of ^1_1H and 0.015 % of ^2_1H . Tritium is an artificial isotope. It does not occur naturally and has only been made in nuclear reactors.

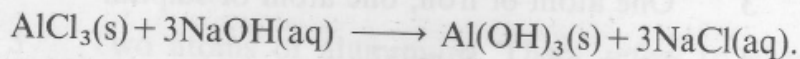
So the relative atomic mass of hydrogen will be the average of the mass numbers of hydrogen and deuterium according to the percentages in which they occur, and the value comes to 1.008. It is close to 1 because protium is by far the most common isotope.

Most of the time, if an element is made of several isotopes, one of them is present in a very large proportion so that when the relative atomic mass is taken to the nearest whole number of that isotope. But not always. Chlorine is one example, and copper is another.

SOMETHING ABOUT MOLE CONCEPT.

One mole of any element is the same as its relative atomic mass in grams.

Equations show how many moles of reactants react together to produce how many moles of product. For example,



states that 1 mole of aluminium chloride reacts with 3 moles of sodium hydroxide to give 1 mole of aluminium hydroxide and 3 moles of sodium chloride. The mole is the quantity of the substance expressed by the relative atomic mass in grams and represented by the symbol of an atom of it.

Atoms combine to form molecules in a compound. One mole of a compound therefore contains one mole of its molecules. The mass of a mole of a compound is therefore the sum of the masses of the number of moles of atoms which constitute one mole of the molecules of the compound. The following examples illustrate how the mass of a mole of a compound can be calculated.

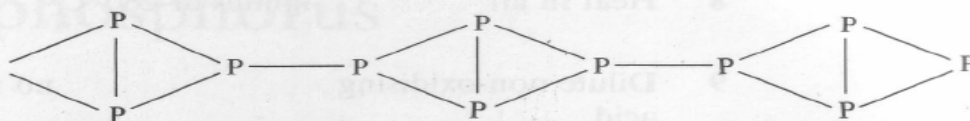
Relative mass of a molecule of water

Relative mass of a mole of water

- | | | | |
|---|--|--|--|
| 1 | Write down the name of the compound. | Water | |
| 2 | Turn the name into a formula. | H_2O | |
| 3 | Write down how many atoms of each element are present in one molecule. | 2 atoms of hydrogen | 1 atom of oxygen |
| 4 | Look up the relative atomic masses of each of the elements in the compound. | H = 1 | O = 16 |
| 5 | Use the information in 3 and 4 to find the total mass of each element present in 1 molecule of water. Add them all together. | for the H:
for the O:
relative mass
of one molecule | $2 \times 1 = 2$
$1 \times 16 = 16 +$
$= \underline{18}$ |

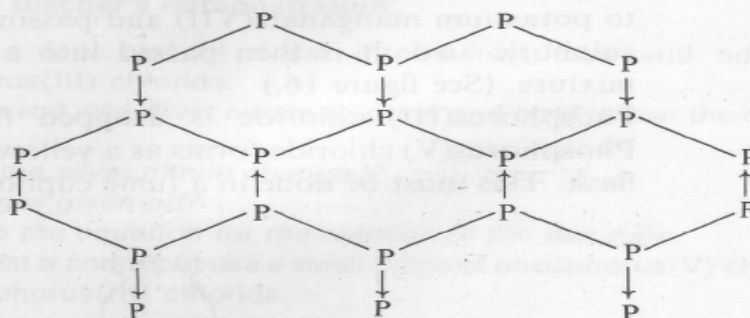
WHICH ARE THE DIFFERENT BETWEEN RED AND BLACK PHOSPHORUS.

Red phosphorus. Red phosphorus is not poisonous and does not catch fire readily. It has a macromolecular structure and is more stable than the white allotrope.



Red phosphorus.

Black phosphorus. When white phosphorus is subjected to high pressures at 200 °C in the absence of air a third allotrope, black phosphorus is formed. Black phosphorus is the most stable of all the allotropes and the most difficult to prepare. It is not normally available in the laboratory. Black phosphorus is a flaky macromolecular solid which conducts electricity and has a higher density than the red variety.



Black phosphorus.

Table 1 Summary of the properties of the red and white allotropes of phosphorus.

		Red phosphorus	White phosphorus
1	Appearance	opaque red, brittle powder	colourless translucent waxy solid which turns yellow
2	Toxicity	not poisonous	poisonous
3	Heat <i>in vacuo</i>	sublimes at 416 °C	melts at 44 °C
4	Density	2.3 g cm ⁻³	1.8 g cm ⁻³
5	Exposure to air	no oxidation	emits a green phosphorescence
6	Solubility in organic solvents	insoluble	soluble

CHAPTER II

ACID-BASE INDICATORS

If you want to know the concentration of any solution, you could use some different methods; one of them is acid-base titration. Here, Acid-Base Indicators are used in order to determine the equivalence point of an acid-base **titration**.

An acid-base indicator, marks the end point of titration by changing color. Although the equivalence point of a titration, defined by the **stoichiometry**, is not necessarily the same as the point (where the indicator changes color), careful selection of the indicator will ensure only negligible error.

It should be noted that another method used a lot for determining the solution concentration is **Potenciometric** Method: Here, the equivalence point is determined by the pH or E (voltage in mv) measurements at different volumes. Afterwards it is possible to plot the **second derivative** of the pH against volume (ml). The peak shows the volume of equivalence point.

The **end point** is defined by the change in color of the indicator. The **equivalence point** is defined by the stoichiometry reaction.

It is important to understand that the equivalence point in an acid-base titration is defined by the stoichiometry, not by the pH. The equivalence point occurs when enough titration has been added to react exactly with all of the acid or base being titrated.

CONCEPTS OF THE KINETIC OF THE REACTION.

From an engineering point of view, reaction kinetics has different functions:

1. Establishing the chemical **mechanism** of a reaction.
2. Obtaining experimental **rate** data.
3. Correlating rate data by equations or other means.
4. Designing suitable reactors
5. Specifying operating conditions, control methods, and auxiliary equipment to meet the technological and economic needs of the reaction processes.

Reactions can be classified in several ways. On the basis of mechanism they may be:

1. **Irreversible**
2. **Reversible**
3. **Simultaneous**
4. **Consecutive**

Further classifications from the point of view of mechanism, the kinetic reactions are classified according to the number of molecules participating in the reaction (**the molecularity**):

1. **Unimolecular**
2. Bimolecular and higher.

Regarding to the reaction order we find other classification:

- First order.
- Second order
- Third order.

With respect to thermal conditions, the principal types are:

1. **Isothermal** at constant volume.
2. Isothermal at constant **pressure**.
3. **Adiabatic**
4. Temperature regulated by heat transfer.

According to the phases involved, reactions are:

1. **Homogeneous** (just one **phase**: gaseous, liquid or solid).
2. **Heterogeneous**.

A major distinction is between reactions that are:

1. Uncatalyzed
2. **Catalyzed** with homogeneous or solid **catalysts**.

Equipment is also a basis for differentiation, namely:

1. **Stirred tanks**, single or in series
2. Tubular reactors, single or in parallel
3. **Reactors** filled with solid particles, inert or catalytic:

There are different **operating** modes:

1. Batch
2. Continuous **flow**
3. **Semibatch** or semiflow

Finally, The Rate Equation Law is generally defined as follow: $r = k C_a^n$

CHAPTER III

LIGNOCELLULOSIC MATERIALS.

Due to increasing concerns about the **greenhouse effect**, ethanol produced by **fermentation** has become important as a potential **fuel** for substituting partially or complementing gasoline. Low production costs are required for making ethanol economically competitive with gasoline. **Lignocellulose** is recognised as the only raw material, with potential for producing large amounts of ethanol at low cost. In many tropical countries, sugarcane **bagasse** is a lignocellulosic material of choice since it is cheap, abundant and it is concentrated at the sugar mill sites and it often represents a disposal problem.

Lignocellulosic materials consist of three major components: cellulose, hemicelluloses and lignin. While cellulose and hemicelluloses are polysaccharides, lignin is an aromatic polymer of phenolic character, whose monomers are three

different phenylpropanoid units. Guaiacyl units derived from coniferyl alcohol and syringyl units derived from sinapyl alcohol are, respectively, the phenylpropanoid units contained in lignins from softwood and hardwood, whereas lignin in grasses (family Gramineae) contains *p*-hydroxyphenyl units derived from *p*-coumaryl alcohol.

Chemical bonds have been reported between lignin and polysaccharides. Phenolic acids, such as ferulic and *p*-coumaric acids, which are **esterified** with L-arabinosyl residues in arabinoxylans, are major lignin monomers that link hemicelluloses and lignin in gramineous plants. Some of the phenolic acids are so intimately associated with the **hemicellulose** fraction that they fail to **crosslink lignin**; therefore they are regarded as hemicellulose components.

In a lignocellulose-to-ethanol process the polysaccharides have to be hydrolysed by means of acids or enzymes in order to obtain a solution of fermentable sugars that could be converted to ethanol. Prior to enzymatic hydrolysis, a **pretreatment** step is required for disrupting the matrix of hemicelluloses and lignin that protect cellulose against enzyme attack. Steam explosion is an extensively studied pretreatment method based on heating the biomass with saturated steam to around 200°C followed by an explosive decompression, while **wet oxidation** is a promising method consisting in treating the material with water and air or oxygen at temperatures above 120°C, leading to a nearly complete solubilisation of hemicellulose fraction, to a significant oxidation and **solubilisation** of lignin and to an increase of the enzymatic convertibility of cellulose. As a result of the partial breakdown and solubilisation of lignin during pretreatment phenolic compounds are formed. The study of the formed phenols is important since several of them have been shown to exert inhibition on the fermentation of **hydrolysates** by ethanologenic **microorganisms**, such as yeast and bacteria. The increased fermentability of laccase-detoxified hydrolysates of willow, spruce and sugarcane bagasse confirmed the inhibitory effect of phenolic compounds.

FERMENTATION

The fermentation of malt **sugars** into beer is a complicated **biochemical process**. It is more than just the conversion of sugar to alcohol, which can be regarded as the primary activity. Total fermentation is better defined as three phases, the Adaptation or Lagtime phase, the Primary or Attenuate phase and a Secondary or Conditioning phase. The yeast do not end Phase 2 before beginning Phase 3, the processes occur in parallel, but the conditioning processes occur more slowly. As the majority of simple sugars are consumed, more and more of the yeast will transition to eating the larger, more complex sugars and early yeast by-products. This is why beer (and wine) improves with age to a degree, as long as they are on the yeast. Beer has been filtered or pasteurized will not benefit from aging.

Lagtime or Adaptation Phase

Immediately after pitching, the yeast begins adjusting to the conditions and it undergoes a period of high growth. The yeast uses any available oxygen in the beginning to facilitate their growth processes. They can use other methods to adapt and grow in the absence of oxygen, but they can do it much more efficiently with oxygen. Under normal conditions, the yeast should proceed through the adaptation phase and

begin primary fermentation within 12 hours. If 24 hours pass without apparent activity, then a new batch of yeast should probably be pitched.

At the beginning of the adaptation phase, the yeast take stock of the sugars, FAN and other nutrients present, and figure out what enzymes and other attributes it needs to adapt to the environment. The yeast uses their own glycogen reserves, oxygen, and wort lipids to synthesize sterols to build up their cell membranes. The sterols are known to be critical for enabling the cell membrane to be permeable to wort sugars and other wort nutrients. Sterols can also be produced by yeasts under poor oxygen conditions from lipids found in wort trub, but that pathway is much less efficient.

Once the cell walls are permeable, the yeast can start metabolizing the amino nitrogen and sugars in the wort for food. Like every animal, the goal of life for the yeast cell is to reproduce. Yeast reproduces asexually by "budding". Daughter cells split off from the parent cell. The reproduction process takes a lot of energy and aerobic metabolic processes are more efficient than anaerobic. Thus, oxygen-rich wort shortens the adaptation phase, and allows the yeast to quickly reproduce to levels that will ensure a good fermentation. When the oxygen is used up, the yeast switch metabolic pathways and begins what we consider to be fermentation - the anaerobic metabolism of sugar to alcohol. This pathway is less energy efficient, so the yeast cannot reproduce as proficently as during the adaptation phase.

The key to a good fermentation is lots of strong healthy yeast- yeast that can get the job done before going dormant due to depleted resources, rising alcohol levels, and old age. As noted, the reproduction rate is slower without oxygen. At some point in the fermentation cycle of the beer, the rate of yeast reproduction is going to fall behind the rate of yeast dormancy. By providing optimum conditions for yeast growth and reproduction in the wort initially, we can ensure that this rate transition will not occur until after the beer has become fully attenuated.

Worts that are underpitched or poorly aerated will ferment slowly or incompletely due to lack of viable yeast. Experienced brewers make a big point about aerating the wort and building up a yeast starter because these practices virtually guarantee enough yeast to do the job well.

Primary or Attenuative Phase

The primary or attenuative phase is marked by a time of vigorous fermentation when the gravity of the beer drops by 2/3-3/4 of the original **gravity** (OG). The majority of the attenuation occurs during the primary phase and can last anywhere from 2-6 days for ales, or 4-10 days for lagers, depending on conditions.

A head of foamy krausen will form on top of the beer. The foam consists of yeast and wort proteins and is a light creamy color, with islands of green-brown gunk that collect and tend to adhere to the sides of the fermentor. The gunk is composed of extraneous wort protein, hop resins, and dead yeast. These compounds are very bitter and if stirred back into the wort, would result in harsh aftertastes. Fortunately these compounds are relatively insoluble and are typically removed by adhering to the sides

of the fermentor as the krausen subsides. Harsh aftertastes are rarely, if ever, a problem.

As the primary phase winds down, a majority of the yeast starts settling out and the krausen starts to subside. If you are going to transfer the beer off of the trub and primary yeast cake, this is the proper time to do so. Take care to avoid **aerating** the beer during the transfer. At this point in the fermentation process, any exposure to oxygen will only contribute to staling reactions in the beer, or worse, expose it to **contamination**.

Many canned kits will advise bottling the beer after one week or after the krausen has subsided. This is not a good idea because the beer has not yet gone through the Conditioning phase. At this time the beer would taste a bit rough around the edges (e.g. yeasty flavors, buttery tones, green apple flavors) but these off-flavors will disappear after a few weeks of conditioning.

Secondary or Conditioning Phase

The reactions that take place during the conditioning phase are primarily a function of the yeast. The vigorous primary stage is over, the majority of the wort sugars have been converted to alcohol, and a lot of the yeast cells are going dormant - but some are still active.

The Secondary Phase allows for the slow reduction of the remaining fermentable. The yeast has eaten most all of the easily fermentable sugars and now start to turn their attention elsewhere. The yeast starts to work on the heavier sugars like **maltotriose**. Also, the yeast clean up some of the **byproducts** they produced during the fast-paced primary phase. But this stage has its dark side too.

Under some conditions, the yeast will also consume some of the compounds in the trub. The "fermentation" of these compounds can produce several **off-flavors**. In addition, the dormant yeast on the bottom of the fermentor begins excreting more amino and fatty acids. Leaving the post-primary beer on the trub and yeast cake for too long (more than about three weeks) will tend to result in soapy flavors becoming evident. Further, after very long times the yeast begin to die and break down - autolysis, which produces yeasty or rubbery/fatty/meaty flavors and aromas. For these reasons, it can be important to get the beer off of the trub and dormant yeast during the conditioning phase.

There has been a lot of controversy within the home brewing community on the value of racking beers, particularly ales, to secondary **fermentor**. Many seasoned home brewers have declared that there is no real taste benefit and that the dangers of contamination and the cost in additional time are not worth what little benefit there may be. While I will agree that for a new brewer's first, low gravity, pale beer that the risks probably outweigh the benefits; I have always argued that through careful transfer, secondary fermentation is beneficial to nearly all beer styles. But for now, I will advise new brewers to only use a single fermentor until they have gained some experience with racking and sanitation.

Leaving an ale beer in the primary fermentor for a total of 2-3 weeks (instead of just the one week most canned kits recommend), will provide time for the conditioning reactions and improve the beer. This extra time will also let more **sediment** settle out before bottling, resulting in a clearer beer and easier pouring. And, three weeks in the primary fermentor is usually not enough time for off-flavors to occur.

Conditioning Processes

The conditioning process is a function of the yeast. The vigorous, primary stage is over, the majority of the wort sugars have been converted to alcohol, and a lot of the yeast is going dormant; but there is still yeast activity. During the earlier phases, many different compounds were produced by the yeast in addition to ethanol and CO₂, e.g., acetaldehyde, esters, amino acids, ketones- diacetyl, pentanedione, dimethyl sulfide, etc. Once the easy food is gone, the yeast start re-processing these by-products. Diacetyl and pentanedione are two ketones that have buttery and honey-like flavors. These compounds are considered flaws when present in large amounts and can cause flavor stability problems during storage. Acetaldehyde is an aldehyde that has a pronounced green apple smell and taste. It is an intermediate compound in the production of ethanol. The yeast reduces these compounds during the later stages of fermentation.

The yeast also produces an array of fusel alcohols during primary fermentation in addition to ethanol. Fusels are higher molecular weight alcohols that often give harsh solvent-like tastes to beer. During secondary fermentation, the yeast **converts** these alcohols to more pleasant tasting fruity **esters**. Warmer temperatures encourage **ester** production.

Towards the end of secondary fermentation, the suspended yeast **flocculates** (settles out) and the beer clears. High molecular weight proteins also settle out during this stage. Tannin/phenol compounds will bind with the proteins and also settle out, greatly smoothing the taste of the beer. This process can be helped by chilling the beer, very similar to the **lagering** process. In the case of ales, this process is referred to as Cold Conditioning, and is a popular practice at most brewpubs and microbreweries. Cold conditioning for a week clears the beer with or without the use of finings. Fining agents, such as isinglass (fish bladders), Polyclar (plastic dust), and **gelatin**, are added to the fermentor to help speed the flocculation process and promote the settling of haze forming proteins and tannins. While much of the emphasis on using finings is to combat aesthetic chill haze, the real benefit of dropping those compounds is to improve the taste and stability of the beer.

CHAPTER IV HEAT AND TEMPERATURE. ASPECTS.

Heat: The total **kinetic energy** of the molecules or atoms composing a substance. The atoms and molecules in a substance do not always move at the same velocity meaning that there is a range of kinetic energy among the atom and molecules.

Temperature: the **average** kinetic energy of individual **atoms** and **molecules**. The distinction between heat and temperature may be made by the following example: A cup of water at 80°C (176°F) is much hotter than a bathtub of water at 30°C (86°F) meaning average kinetic energy of individual water molecules at 80°C is greater than at 30°C. On the other hand the bathtub has the greater volume of water. It contains more total kinetic molecular energy than the cup of water. As a result, a cup of water will cool down at room temperature much more rapidly than the **bathtub** of water. Much more heat energy must be removed from the bathtub water than from the cup of water in order to cool it at the same temperature.

As a sample of air gains or loses heat, the amount of gained or lost **heat** is used for changes in temperature, phase of water, or volume of the air sample, or combination of these.

For scientific purposes, temperature is described in terms of the *Celsius scale*, which was first proposed by the Swedish astronomer Andres Celsius in 1736. It has 100°C interval between melting point of ice and boiling point of pure water. An alternative scale is *Fahrenheit scale*, which was introduced by German physicist (Gabriel Fahrenheit in 1714). The conversion between Celsius and Fahrenheit scale is as follows:

$$F \text{ degree} = (1,8 * ^\circ C) + 32$$

$$C \text{ degree} = (^\circ F - 32) / 1.8$$

Absolute zero: The theoretical temperature at which a body emits no electromagnetic radiation and all molecular action ceases. It is equivalent to -273.15°C and -459.67°F, and 0°K, *Kelvin scale*, which was introduced by Scottish physicist Lord Kelvin in 1844. Kelvin scale has 100° interval between melting point of ice (273.15 K) and boiling point of water (373.15 K). The conversion between the Kelvin scale and Celsius and Fahrenheit scales is given as follows:

$$K = ((F - 32) / 1.8) + 273.16$$

$$K = ^\circ C + 273.16$$

Thermometer: the instrument that monitors the changes in air temperature. A liquid-in-glass thermometer uses either mercury which freezes at -39°C or alcohol which freezes at -117°C. As the air temperature rises, the liquid in the glass tube expands and rises, while the liquid contracts and drops in the tube as the temperature decreases.

Maximum thermometer, reads maximum temperature over a specified period, usually uses mercury as a liquid and has small construction in the tube just above the bulb.

Minimum thermometer, reads minimum temperature over a specified period, uses alcohol as a liquid and has a index marker that is free to slide back or forth within the liquid.

Bimetallic thermometer consists of two different metals (usually brass and iron) that are welded together side by side and are linked to a pointer and a calibrated dial via a series of gears or levers. The pointer may be linked to a pen and a clock-driven drum to give continuous trace of temperature variations with time. The instrument is called *thermograph*. A **thermistor thermometer**, an electrical conductor whose resistance changes as the temperature fluctuates, is used in **radiosondes**.

Modes of heat transfer (heat transfer).

There are three fundamental types of heat transfer: conduction, convection, and radiation. All three types may occur at the same time, and it is advisable to consider the heat transfer by each type in any particular case.

Conduction is the transfer of heat from one part of a body to another part of the same body, or from one body to another in physical contact with it, without appreciable displacement of the **particles** of the body.

Convection is the transfer of heat from one point to another within a fluid, gas, or liquid by the mixing of one portion of the fluid with another. In natural convection, the motion of the fluid is entirely the result of differences in **density** resulting from **temperature** differences; in forced convection, the motion is produced by mechanical means. When the forced velocity is relatively low, it should be realized that “free-convection” factors, such as density and temperature difference, may have an important influence.

Radiation is the transfer of heat from one body to another, not in contact with it, by means of wave motion through space.

SUCCESSFULLY DESIGNED EXPERIMENTS.

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Design of experiments (DOE) provides a powerful means to achieve breakthrough improvements in product quality and process efficiency. This leads to increased market share, decreased costs, and big gains in profit. So why don't more manufacturers use design of experiments (DOE)? In some cases it's simple ignorance, but even when companies provide proper training, experimenters resist DOE because it requires planning, discipline and the use of statistics. Fear of statistics is widespread, even among highly educated scientists and managers. Quality professionals can play a big role in helping their colleagues overcome these barriers.

Using DOE successfully depends on understanding eight fundamental concepts.

To illustrate these keys to success, we'll follow two case studies:

☐ Increasing the life of a bearing

☐ Reducing shrinkage of **plastic** parts from an injection molding process

The focus will be on 2-level factorial design, where each input variable is varied at high (+) and low (~) levels. These designs are very simple, yet extremely powerful. For example, Figure 1 shows the results for a 2-level design on 3 factors affecting bearing life. Note the large increase at the upper right corner of the cube. In this case two **factors** interact to produce an unexpected breakthrough in product quality. One-factor-at-a-time (OFAT) experimentation will never Full factorials are much more efficient than

OFAT, because they make use of **multivariate design**. It's simply of matter of parallel processing (with factorial design) versus serial processing (with OFAT). Furthermore, you don't need to run the full number of 2-level combinations, particularly when you get to 5 or more factors. By making use of fractional designs, the 2-level approach can be extended to many factors. Therefore, these DOEs are ideal for screening many factors to identify the vital few that significantly affect your response. The injection molding case will demonstrate the use of fractional 2-level design.

The first decision before designing an experiment is "what is the objective, or purpose, of this study?" The focus of the study may be to screen out the factors that are not critical to the process, or it may be to optimize a few critical factors. A well-defined objective leads the experimenter to the correct DOE. For example, in the initial stage of process development or troubleshooting, the appropriate design choice is a fractional two-level factorial. This DOE screens a large number of factors in a minimal **number of runs**. However, if the process is already close to optimum conditions, then a response surface design may be most appropriate. It will explore a few factors over many levels. If you do not identify the objectives of a study, you may pay the consequences:

1. trying to study too many or too few factors
2. not measuring the correct responses
3. arriving at conclusions that are already known

In essence, vague objectives lead to lost time and money, as well as feelings of frustration for all involved. Identifying the objective up-front builds a common understanding of the project and expectations for the outcome.

In our case study of the injection molder, management wants to reduce variation in the **shrinkage** of their parts. If the shrinkage can be stabilized, then mold dimensions can be adjusted so the parts can be made consistently.

The factors and levels to be studied are:

FACTOR	NAME	UNITS	LOW LEVEL	HIGH LEVEL
A:	Mold Temp	Degrees F	130	180
B:	Holding Pressure	PSIG	1200	1500
C:	Booster Pressure	PSIG	1500	1800
D:	Moisture Percent	%	0.05	0.15
E:	Screw Speed	Inches/sec	1.5	4.0
F:	Cycle Time	seconds	25	30
G:	Gate Size	Mils	30	50

The experimenters have chosen a 2-level **factorial design** with 32 runs. A full set of combinations would require 128 runs (2⁷) so this represents a 1/4 fraction.

Design of experiments is a very powerful tool that can be utilized in all manufacturing industries. The keys to success are:

1. Set good objectives.
2. Measure responses quantitatively.
3. Replicate to dampen uncontrollable variation.
4. Randomize the run order.
5. Block out known sources of variation.
6. Know which effects (if any) will be aliased.

7. Do a sequential series of experiments.

8. Always confirm critical findings.

Quality managers who encourage use of DOE, and promote these keys, will greatly increase the chances for making breakthrough improvements in product quality and process efficiency.

MATERIAL SAFETY DATA SHEET. SULFUR TRIOXIDE, STABILIZED, 99%

Section 1 - Chemical Product and Company Identification

Name: Sulfur trioxide, stabilized, 99%

Synonyms: Sulfan(R); Sulfuric anhydride. Stabilizer is <0.3% dimethyl sulfate.

Powerful sulfonating **agent**. May contain low-melting solid polymer, the formation of which is unavoidable.

CAS#	Chemical Name	Percent
7446-11-9	Sulfur trioxide	99

Appearance: clear, colorless to pale yellow liquid.

Danger! Sulfur trioxide reacts violently with water forming sulfuric acid. Causes eye and skin burns. Causes digestive and respiratory tract burns. May be fatal if inhaled. Do not freeze. Hygroscopic (absorbs moisture from the air).

Target Organs: Eyes, skin, mucous membranes.

Potential Health Effects

Eye: Causes eye burns.

Skin: Causes skin burns.

Ingestion: Causes gastrointestinal tract burns.

Inhalation: May be fatal if inhaled. Causes chemical burns to the respiratory tract.

Chronic: Workers chronically exposed to sulfuric acid mists may show various lesions of the skin, tracheobronchitis, stomatitis, conjunctivitis, or gastritis. Occupational exposure to strong inorganic acid mists containing sulfuric acid is carcinogenic to humans.

Section 4 - First Aid Measures

Eyes: In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical aid immediately.

Skin: In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Get medical aid immediately. Wash clothing before reuse.

Ingestion: If swallowed, do NOT induce vomiting. Get medical aid immediately. If victim is fully conscious, give a cupful of water. Never give anything by mouth to an unconscious person.

Inhalation: **POISON** material. If inhaled, get medical aid immediately. Remove victim to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen.

Notes to Physician: Treat symptomatically and supportively.

Section 5 - Fire Fighting Measures

General Information: As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and full protective gear. React with most metals in the presence of moisture, liberating extremely flammable hydrogen gas. React with steam to form corrosive, toxic fumes of sulfuric acid. Approach fire from upwind to avoid hazardous vapors and toxic decomposition products. Strong dehydrating agent, which may cause ignition of finely divided materials on contact. Oxides of sulfur may be produced in fire. SO₃ chars many organic substances due to its avidity for water. On contact with wood shavings, the heat produced by **dehydration** is sufficient to cause fire.

Extinguishing Media: Do NOT use water directly on fire. Use carbon dioxide or dry chemical. Do NOT get water inside containers.

Flash Point: Not available.

Autoignition Temperature: Not available.

Explosion Limits, Lower: Not available.

Upper: Not available.

Section 6 - Accidental Release Measures

General Information: Use proper personal protective equipment as indicated in Section 8.

Spills/Leaks: Avoid runoff into storm sewers and ditches which lead to waterways. Clean up spills immediately, observing precautions in the Protective Equipment section. Absorb spill using an absorbent, non-combustible material such as earth, sand, or vermiculite. Do not use combustible materials such as sawdust. Provide ventilation. Do not get water inside containers. Evacuate unnecessary personnel. Approach spill from upwind.

Section 7 - Handling and Storage

Handling: Wash thoroughly after handling. Remove contaminated clothing and wash before reuse. Do not get in eyes, on skin, or on clothing. Keep container tightly closed. Do not allow contact with water. Discard contaminated shoes. Do not breathe vapour. Store it absolutely dry. Do not use with metal spatula or other metal items. Use only with adequate ventilation or respiratory protection.

Storage: Keep from freezing. Keep container closed when not in use. Store it in a cool, dry well-ventilated area away from incompatible substances. Store it at around 20°C. Store it in a suitable container in a dry area above the substance's freezing point. Do NOT freeze.

EVOLUTION OF QUALITY

Some thoughts on the evolution of quality engineering An introduction to quality engineering

Recently, Taguchi methods have become very popular among industries worldwide. Many academic research papers and industrial application reports have been published under the title "Taguchi methods". In fact, the so-called "Taguchi methods" is a collective term. It consists of system of **experiment design**, quality engineering (QE), business data analysis, and divisional evaluation **system** and pattern recognition. Furthermore, QE can be divided into online QE and off-line QE. Online QE is in contrast with traditional statistical process control (SPC) and off-line QE is in contrast with classical design and analysis of experiments. The difference between online and off-line QE is that activities of the former are done along mass production lines while that of the latter are done prior to mass production. There are three steps in off-line QE, i.e. system design, parameter design and tolerance design. What most people in North America call robust design refers to parameter design and tolerance design together? This is also the focus of discussions among statisticians and quality specialists. In this paper, QE refers to off-line QE in Taguchi methods.

Taguchi defines quality of a product process as the loss to society. Losses are incurred because performances of products deviate from their targets (ideal function). And deviation is caused by noise. Noises are uncontrollable variables, such as environmental factors (temperature, **humidity, dust, magnetic**, etc.), variation within components and deterioration (wear-out). Therefore, noises are always there and we can never eliminate them. So are losses. The best we can do is to make our products/processes "strong" enough to be less sensitive to the effects of noises. That is, through minimization of loss, we obtain a robust product/ process.

In system design, design engineers examine a variety of architectures and technologies for achieving the desired function of the product and select the most suitable ones for the product/process. Engineering expertise plays a big part here. Next, in parameter design, designers start with the lowest possible cost and try to determine the best settings for each control factor to minimize the sensitivity to noises. Taguchi suggests using two orthogonal arrays (control array and noise array) to study the effects of noises combinations on the various combinations of control factors. If, at the end of parameter design the quality loss is acceptable, we have a design with the lowest cost. Otherwise, we have to go to the third step - tolerance design. In tolerance design, a trade-off is made between **reduction** in the quality loss and increase in **manufacturing cost**.

REFERENCES

1. Anderson, M. J., Whitcomb, P. J. [1997], "Software Sleuth Solves Engineering Problems", *Machine Design*, 6/5/97.
2. Anderson, M. J., Whitcomb, P. J. [1997], "Breakthrough Improvements with Experiment Design", *Rubber and Plastics News*, 6/16/97.
3. Box, Hunter and Hunter [1978], *Statistics for Experimenters*, John Wiley & Sons.
4. Watts, E. G. [1997], "Explaining Power Using Two-Level Factorial Designs", *Journal of Quality Technology*, Vol. 29, No. 3, (July).
5. Fergusson, J (1985), "CXC Chemistry", Oxford University.

ANNEXES

How we can write a Paper?

Makromol. Chem., Rapid Commun. **14**, 735–740 (1993)

735

Preparation of a novel polyampholyte from chitosan and citric acid

Synthesis of citrylated chitosan

Chitosan powder (5 g) dispersed in water (245 g) was dissolved by adding citric acid up to a pH lower than 2,5 (approximately 20 g). The solution was poured into two Petri dishes (14,5 cm diameter) and dried in a vacuum oven at 80 °C. The chitosan citrate films formed were heated at 100 °C in vacuum ($6 \cdot 10^{-2}$ mmHg), thus promoting dehydration of the salt with formation of the corresponding amide linkage. In order to follow the course of the reaction, samples were periodically taken and their solubility

In the intermediate region of the pH interval studied, precipitation of the polymer is observed. The isoelectric point of this polyampholyte should lie in this zone where, as a consequence of the electroneutrality of the macromolecule, the polymer becomes insoluble.

Conclusions

A novel polyampholyte was prepared via direct reaction of chitosan and citric acid in solid phase. In this case substitution degrees higher than 30% can be achieved. The potentiometric and viscometric behaviour of its solutions are typical of this type of substance. Further investigations are in course.

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- 1) R. A. A. Muzzarelli, F. Tanfani, S. Mariotti, M. Emanuelli, *Carbohydr. Polym.* **2**, 145 (1982)
- 2) R. A. A. Muzzarelli, *Carbohydr. Polym.* **8**, 1 (1988)
- 3) R. A. A. Muzzarelli, M. Weckx, O. Filippini, C. Lough, *Carbohydr. Polym.* **11**, 307 (1989)
- 4) S. Hirano, Y. Nishiguchi, *Carbohydr. Polym.* **5**, 13 (1985)
- 5) R. A. A. Muzzarelli, "Amphoteric Derivatives of Chitosan and their Biological Significance" in: *Chitin and Chitosan*, G. Skjåk-Braek, T. Anthonsen and P. Sandford, Eds., Elsevier Sci. Publ., London 1989, p. 87
- 6) R. A. A. Muzzarelli, A. Zatoni, *Int. J. Biol. Macromol.* **8**, 137 (1986)
- 7) G. A. F. Roberts, J. G. Domzsy, *Int. J. Biol. Macromol.* **4**, 374 (1982)
- 8) A. Domard, C. Gey, M. Rinaudo, C. Terrasin, *Int. J. Biol. Macromol.* **9**, 233 (1987)
- 9) M. Terbojevich, C. Carraro, A. Cosani, B. Focher, A. M. Naggi, G. Torri, *Makromol. Chem.* **190**, 2847 (1989)
- 10) C. Tanford, "Physical Chemistry of Macromolecules", Wiley, New York 1961, pp. 550–573

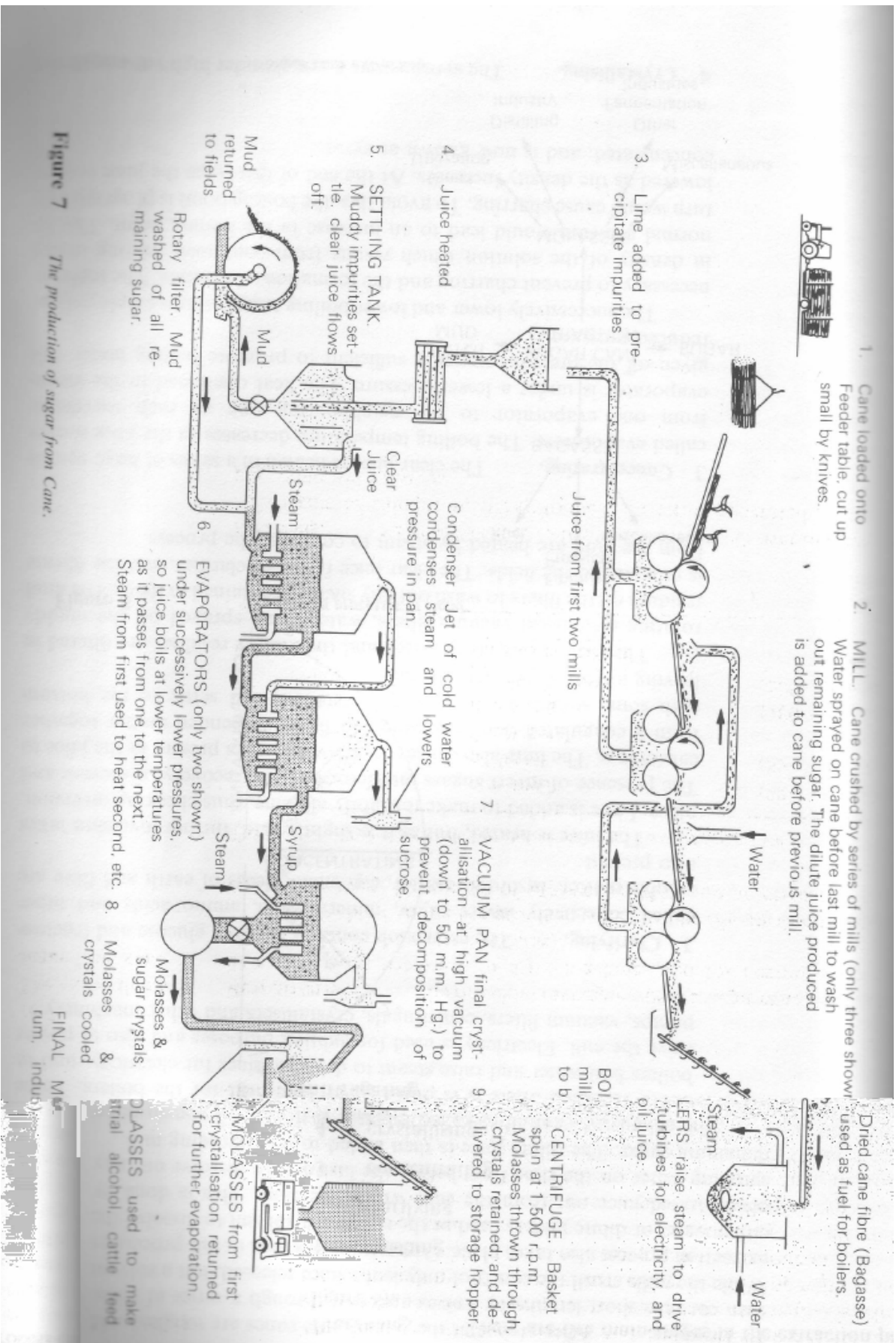


Figure 7 The production of sugar from Cane.