GATE Material for Chemical Engineering

General Chemical Engineering Concepts

What is a Chemical Engineer?

It is true that chemical engineers are **comfortable with chemistry**, but they do much more with this knowledge than just make chemicals. In fact, the **term "chemical engineer"**is not even intended to describe the type of work a chemical engineer performs. Instead it **is meant to reveal what makes the field different** from the **other branches of engineering**.

All **engineers employ mathematics, physics, and the engineering art to overcome technical problems in a safe and economical fashion**. Yet, it is the chemical engineer alone that draws upon the vast and powerful science of chemistry to solve a wide range of problems. The strong technical and social ties that bind chemistry and chemical engineering are unique in the fields of science and technology. This marriage between chemists and chemical engineers has been beneficial to both sides and has rightfully brought the envy of the other engineering fields.

The breadth of scientific and technical knowledge inherent in the profession has caused some to describe the chemical engineer as the "**universal engineer**." Yes, you are hearing me correctly; despite a title that suggests a profession composed of narrow specialists, chemical engineers are actually extremely versatile and able to handle a wide range oftechnical problems.

**So What Exactly Does This "Universal Engineer" Do?**

During the past Century, chemical engineers have made tremendous contributions to our standard of living. To celebrate these accomplishments, the American Institute ofChemical Engineers (AIChE) has compiled a list of the "**10 Greatest Achievements of Chemical Engineering.**" These triumphs are summarized below:

**The Atom, as Large as Life:**

Biology, medicine, metallurgy, and power generation have all been revolutionized by our ability to **split the atom** and**isolate isotopes**. Chemical engineers played a prominent role in achieving both of these results. Early on facilities such as DuPont's Hanford Chemical Plant used these techniques to bring an abrupt conclusion to **World War II** with the production of the atomic bomb. Today these technologies have found uses in more peaceful applications. **Medical doctors**now use isotopes to monitor bodily functions; quickly identifying clogged arteries and veins. Similarly **biologists**gain invaluable insight into the basic mechanisms of life, and**archaeologists** can accurately date their historical findings.

**The Plastic Age:**

The 19th Century saw enormous advances in **polymer chemistry**. However, it required the insights of chemical engineers during the 20th Century to make mass produced polymers a viable **economic reality**. When a plastic called**Bakelite** was introduced in 1908 it sparked the dawn of the "Plastic Age" and quickly found uses in electric insulation, plugs & sockets, clock bases, iron cooking handles, and fashionable jewelry. Today plastic has become so common that we hardly notice it exists. Yet nearly all aspects of modern life are positively and profoundly impacted by plastic.

**The Human Reactor:**

Chemical engineers have long studied complex chemical processes by breaking them up into smaller "**unit operations.**" Such operations might consist of heat exchangers, filters, chemical reactors and the like. Fortunately this concept has also been applied to the human body. The results of such analysis have helped improve **clinical care**, suggested improvements in **diagnostic and therapeutic devices**, and led to mechanical wonders such as **artificial organs**. Medical doctors and chemical engineers continue to work hand in hand to help us **live longer fuller lives**.

**Wonder Drugs for the Masses:**

Chemical engineers have been able to take small amounts of**antibiotics** developed by people such as Sir Arthur Fleming (who discovered penicillin in 1929) and **increase their yields**several thousand times through **mutation** and special**brewing** techniques. Today's **low price, high volume,** drugs owe their existence to the work of chemical engineers. This ability to bring once scarce materials to **all members of society** through industrial creativity is a defining characteristic of chemical engineering.

**Synthetic Fibers, a Sheep's Best Friend:**

From blankets and clothes to beds and pillows, synthetic fibers keep us **warm**, **comfortable**, and provide a **good night's rest**. Synthetic fibers also help **reduce the strain** on natural sources of **cotton and wool**, and can be tailored to specific applications. For example; **nylon stockings** make legs look young and attractive while **bullet proof vests** keep people out of harm's way.

**Liquefied Air, Yes it's Cool:**

When air is cooled to very low temperatures (about **320 deg F below zero**) it condenses into a liquid. Chemical engineerscan then separate out the different components. The purified**nitrogen** can be used to recover petroleum, freeze food, produce semiconductors, or prevent unwanted reactions while**oxygen** is used to make steel, smelt copper, weld metals together, and support the lives of patients in hospitals.

**The Environment, We All Have to Live Here:**

Chemical engineers provide **economical answers** to clean up yesterday's **waste** and prevent tomorrow's **pollution**.**Catalytic converters**, reformulated **gasoline**, and smoke stack **scrubbers** all help keep the world clean. Additionally,chemical engineers help reduce the strain on natural materials through **synthetic replacements**, more **efficient processing**, and new **recycling** technologies.

**Food, "It's What's For Dinner":**

Plants need large amounts of **nitrogen**, **potassium**, and**phosphorus** to grow in abundance. Chemical **fertilizers** can help provide these nutrients to crops, which in turn provide us with **a bountiful and balanced diet**. Fertilizers are especially important in certain regions of Asia and Africa where food can sometimes be scarce . Advances in **biotechnology** also offer the potential to further increase worldwide food production. Finally, chemical engineers are at the forefront of **food processing** where they help create better tasting and most nutritious foods.

**Petrochemicals, "Black Gold, Texas Tea":**

Chemical engineers have helped develop processes like**catalytic cracking** to **break down** the complex organic molecules found in crude oil into much simpler species. These**building blocks** are then separated and recombined to form many useful products including: **gasoline**, **lubricating oils**,**plastics**, **synthetic rubber**, and **synthetic fibers**. Petroleum processing is therefore recognized as an **enabling technology**, without which, much of modern life would cease to function

**Running on Synthetic Rubber:**

Chemical engineers played a prominent role in developing today's synthetic rubber industry. During **World War II**, synthetic rubber capacity suddenly became of paramount importance. This was because modern society runs on rubber.**Tires**, **gaskets**, **hoses**, and **conveyor belts** (not to mention**running shoes**) are all made of rubber. Whether you drive, bike, roller-blade, or run; odds are you are running on rubber.

**Chemical Engineering Today & Tomorrow**

The "**Big Four**" engineering fields consist of **civil, mechanical, electrical, and chemical engineers.** Of these, **chemical engineers** are **numerically** the **smallest**group. However, this relatively small group holds a very prominent position in many industries, and chemical engineersare, on average, the **highest paid** of the "Big Four". Additionally, many chemical engineers have found their way into **upper management**. A chemical engineer is either currently, or has previously, occupied the CEO position for**: 3M, Du Pont, General Electric, Union Carbide, Dow Chemical, Exxon, BASF, Gulf Oil, Texaco, and B.F. Goodrich**. Even a former director of the **CIA**, John M. Deutch, was a chemical engineer by training.

More typically, chemical engineers concern themselves with the chemical processes that turn **raw materials into valuable products**. The necessary skills encompass all aspects of design, testing, scale-up, operation, control, and optimization, and require a detailed understanding of the various "**unit operations**", such as distillation, mixing, and biological processes, which make these conversions possible. Chemical engineering science utilizes **mass, momentum, and energy transfer** along with **thermodynamics** and **chemical kinetics** to analyze and improve on these "unit operations."

Today there are around **70,000 practicing chemical engineers** in the United States (57,000 of these are AIChE members) . During the entire **history of the profession**there have been only about **135,000 American chemical engineers** (including those alive today). This means that**more than a half** of all the chemical engineers who have ever existed are **contributing to society right now**! Chemical engineering is not a profession that has to dwell on the achievements of the past for comfort, for its greatest accomplishments are yet to come.

History Of Chemical Engineering

The Past & Present

Setting the Stage for a New Profession

Setting the Stage for a New Profession, Chemical Engineering in 1888.

For all intents and purposes the **chemical engineering**profession **began in 1888**. While, the term "chemical engineer" had been floating around technical circles throughout the 1880's, there was no formal education for such a person. The "chemical engineer" of these years was either a mechanical engineer who had gained some knowledge of chemical process equipment, a chemical plant foreman with a lifetime of experience but little education, or an applied chemist with knowledge of large scale industrialchemical reactions.

An effort in 1880, by **George Davis** (see Davis below), to unite these varied professionals through a "**Society ofChemical Engineers**" proved unsuccessful. However, this muddled state of affairs was changed in 1888, when**Professor Lewis Norton** of the **Massachusetts Institute of Technology** introduced "**Course X**" (ten), thereby unitingchemical engineers through a **formal degree**. Other schools, such as the **University of Pennsylvania** and **Tulane University**, quickly followed suit adding their own four yearchemical engineering programs in 1892 and 1894 respectively.

The Story: Early Industrial Chemistry

Chemical Engineering Needed in England

As the **Industrial Revolution** (18th Century to the present) steamed along certain basic chemicals quickly became necessary to sustain growth. **Sulfuric acid** was first among these "industrial chemicals". It was said that a nation'sindustrial might could be gauged solely by the vigor of its sulfuric acid industry (C1). With this in mind, it comes as no surprise that **English industrialists** spent a lot of **time**,**money**, and **effort** in attempts to improve their processes for making sulfuric acid. A slight savings in production led to large profits because of the vast quantities of sulfuric acid consumed by industry.

Sulfuric Acid Production

To create sulfuric acid the long used (since 1749), and little understood, **Lead-Chamber Method** required air, water, sulfur dioxide, a nitrate, and a large lead container. Of these ingredients the nitrate was frequently the most expensive. This was because during the final stage of the process, nitrate (in the form of nitric oxide) was **lost to the atmosphere**thereby necessitating a make-up stream of fresh nitrate. This additional nitrate, in the form of **sodium nitrate** (see Nitrates below), had to be imported all the way from **Chile**, making it very **costly** indeed!

In 1859, **John Glover** helped solve this problem by introducing **a mass transfer tower to recover some of this lost nitrate**. In his tower, sulfuric acid (still containing nitrates) was trickled downward against upward flowing burner gases. The flowing gas absorbed some of the previously lost nitric oxide. Subsequently, when the gases were recycled back into the lead chamber the nitric oxide could be re-used.

The **Glover Tower** represented the trend in many chemical industries during the close of the 19th Century. **Economic forces were driving the rapid development and modernization of chemical plants**. A well designed plant with innovative chemical operations, such as the Glover Tower, often meant the difference between success and failure in the highly competitive chemical industries. (see Sulfuric Acid below, or FIGURE: SULFURIC ACID GROWTH).

Alkali & The Le Blanc Process

Another very competitive (and ancient) chemical industry involved the manufacture of **soda ash** (Na_2CO_3) and**potash** (K_2CO_3) (see Carbonates below) . These **Alkali compounds** found use in a wide range of products including**glass**, **soap**, and **textiles** and were therefor in tremendous demand. As the 1700's expired, and English trees became scarce, the only native source of soda ash remaining on the British Isles was **kelp** (seaweed) which irregularly washed up on its shores. Imports of Alkali, from America in the form of wood ashes (potash) or Spain in the form of barilla (a plant containing 25% alkali) or from soda mined in Egypt, were all very expensive due to high shipping costs.

Fortunately for English coffers (but unfortunately for the English environment) this dependence on external soda sources ended when a Frenchman named Nicholas Le Blanc invented a process for converting common **salt into soda ash**. The **Le Blanc Process** (see Le Blanc below) was adopted in England by 1810 and was continually improved over the next 80 years through elaborate engineering efforts. Most of this labor was directed at recovering or reducing the terrible byproducts of the process. Hydrochloric acid, nitrogen oxides (see Glover Tower above), sulfur, manganese, and chlorine gas were all produced by the Le Blanc process, and because of these chemicals many manufacturing sites could easily be identified by the ring of dead and dying grass and trees.

A **petition against the Le Blanc Process** in 1839 complained that "the gas from these manufactories is of such a deleterious nature as to blight everything within its influence, and is alike baneful to health and property. The herbage of the fields in their vicinity is scorched, the gardens neither yield fruit nor vegetables; many flourishing trees have lately become rotten naked sticks. Cattle and poultry droop and pine away. It tarnishes the furniture in our houses, and when we are exposed to it, which is of frequent occurrence, we are afflicted with coughs and pains in the head...all of which we attribute to the Alkali works." Needless to say, many people strove to replace the Le Blanc Process with something less offensive to nature and mankind alike.

A Century of Contributions

While **chemical engineering** was **first conceptualized** in**England** over a Century ago, its **primary evolution**, both educationally and industrially, has occurred in the **United States**. After an early **struggle for survival**, the profession**emerged from** under its **industrial chemistry heritage**with the **help of** the **unit operations** concept.

However, the **metamorphosis** of chemical engineering did not stop there. The addition of **material and energy balances**, **thermodynamics**, and **chemical kinetics**brought the profession closer to something a modernchemical engineer would recognize. With stress

on**mathematical competence**, as necessitated by **chemical reactor modeling** and a more detailed examination of**transport phenomena**, chemical engineering continues to broaden in scope. A further requirement in **computer literacy**, as necessary for **process control**, allows today'schemical engineer to be much more efficient with their time.

Along the way, this **changing educational emphasis** has helped the chemical engineer keep up with the **changingindustrial needs** and continue to make significant**contributes to society** . Today their broad background has opened doors to many **interdisciplinary areas** such as**catalysis**, **colloid science**, **combustion**,**electrochemical engineering**, **polymer technology**,**food processing**, and **biotechnology**. The **future** ofchemical engineering seems to lie with these **continuing trends** towards greater **diversity**.

The Story: Chemical Engineering Evolution

World War I

Outbreak of Hostilities

On June 28, **1914**, crowds of people lined the streets of**Sarajevo**, the capital of **Bosnia** (then a province of Austria-Hungary), in hopes of seeing the **Archduke FrancisFerdinand** and his wife **Sofia**. A young student, **Gavrilo Princip**, leapt from the crowd and **assassinated** the**Archduke and his wife**. Suspecting the **plot** originated in**Serbia**, **Austria-Hungary** (including Bosnia) **declared war**on the small country. By the end of 1914, **Europe** was **swept**into the horrendous conflict that would become **World War I**(maybe we should be more concerned with the ongoing hostilities between the Bosnians and Serbians!)

The American Situation

Prior to the war, **Germany** had **reigned supreme** in**organic chemistry** and **chemical technology**. It was said in 1905 that **America lagged fifty years behind** the Germans in organic chemical processing (H7). Even America's chemistry and chemical engineering **professors** had been primarily trained in **German Universities**, and a working knowledge of the **German language** was essential to keep up with the **latest chemical advances**. All in all,**America's chemical industry** was too **narrow**, concentrating in only a few **high volume chemical products**, such as sulfuric acid.

America's Opportunity

As war raged in Europe, the **America found itself isolated**from Germany. British blockades prevented valuable **dyes**and **drugs**, produced only in Germany, from reaching American shores. Suddenly the **American chemical industry** was given the opportunity to **enter these markets** without foreign competition.

The Problem

However, **chemical engineers** were **not entirely ready**for this turn of events. Their **education** had consisted primarily of instruction in **engineering practice** and**industrial chemistry**. This memorization of existing chemical processes was fine for supervising established chemical plants, but left them at a great **disadvantage** when faced with tackling **entirely new problems**.

Faced with this challenge, how could the technological know-how concerning one set of chemicals be transferred to a new set? The answer came in 1915, when **Arthur Little**introduced the "**unit operations**" concept. With it, chemical engineers where trained about **chemical processes** in a more **abstract** manner. Their **expertise** became**independent** of the **actual chemicals** involved, allowing the **rapid establishment** of **new industries**. In short,*education had responded to the needs of industry*.

The Industry of War

In **1917**, after loosing several ships and many lives, the**United States declared war** on Germany and her Allies. One of the **first actions** of the U.S. Government was to ensure our **chemists and chemical engineers** did **not die in the trenches** as had happened to our European counterparts. **Instead**, they were enlisted to **create the materials necessary to wage war**. Suddenly, united by a**common foe**, America's chemical industries began**cooperating** instead of competing. This cooperation would build the **ammonia plants** that produced the **explosives**(and **fertilizers**) that helped win the war (see NITROGEN: FOOD OR FLAMES).

World War II

Hostilities Re-Ignite

On September 18, 1931, **Japan invaded Manchuria**. Eight years later, on September 1, 1939, **Germany invaded Poland** and war again raged on the European continent. With Japan's infamous **bombing of Pearl Harbor**, on December 7, 1941, **America** was once again **thrust into a World War**.

Synthetic Rubber

The **importance** of rubber in warfare was demonstrated by the **Germans** in **World War I**. The Germans had been **cut off** from their foreign **rubber supply** by the **British blockade**. Without rubber their **trucks** ran out of **tires** while their **troops** had to go without walking **boots**. In an effort to salvage the situation, Germany began experimenting with**synthetic rubber.** However, they **never** found a formula that **worked well enough** and could be produced in large enough quantities.

Similarly, in the opening days of **World War II, Japan**rapidly **captured** rubber producing lands in the **Far East**,**depriving America of 90%** of its natural **rubber** sources. Suddenly America found itself in the same undesirable position that had confronted Germany forty years before.

However, with the help of their new educational emphasis on the underlying principles of chemistry and engineering as opposed to the gross memorization of existing industrialchemical reactions, American chemical engineers were in a position to make great contributions to the synthetic rubber effort. The **unit operations** concept, combined with **mass and energy balances** and **thermodynamics** (which had been stressed in the 30's), allowed the rapid **design, construction, and operation** of **synthetic rubber plants**.Chemical Engineers now had the training to build industries from the ground up. With funds from the government, the chemical industry was able to increase synthetic **rubber production** over a **hundred fold**. This synthetic rubber found uses in tires, gaskets, hoses, and boots; all of which contributed to the war effort.

High Octane Gasoline

As **German tanks and bombers** swept across Europe using**Blitzkrieg** tactics, it became evident that World War II would be a **highly mechanized conflict**. The Allies needed tanks, fighters, and bombers all supplied with **large quantities** of**high quality gasoline**. In supplying this fuel the American petroleum industry was stretched to its limit

However, the development of **Catalytic Reforming** in 1940 by the Standard Oil Company (Indiana) gave the **Allies an advantage**. The reforming process produced **high-octane fuel** from **lower grades of petroleum** (it also made**Toluene** for **TNT**). Because of the performance edge given by better fuel, **Allied planes** could successfully **compete**against **German & Japanese fighters**.

The Atomic Bomb

In the early 1900's **scientists** were busy **exploring the atom**. Einstein's mass-energy equivalence ($E = m c^2$) showed that **matter** contained **tremendous energy**. By 1939 many scientists had succeeded in **splitting atoms** of uranium and some envisioned the possibility of a chain reaction. In 1942, **Fermi** and his co-workers produced the first **man-made chain reaction** under the **University of Chicago**. The success proved that an atomic weapon was possible, and the **Manhattan Project** was soon underway. However, despite these early successes, **enormous technical obstacles** still lay ahead.

Only certain materials underwent **fission** rapidly enough to be considered for an atomic bomb. **Uranium 235**, a very scarce from of uranium (only 0.7% of uranium is 235), and**plutonium**, an element that did not exist naturally, were two possible candidates. However, both elements were**exceeding rare** (or nonexistent) and had only been produced on **tiny laboratory scales**. For example, in 1942 only a milligram of Plutonium (1/28,000th of an ounce) was in existence.

Late in 1942, General Leslie R. Groves approached **Du Pont**to ask if they could build and operate a **plutonium production plant**. The company accepted the challenge, but due to intense secrecy, not even its top-level people new the whole story. During the next three years the "**Hanford Engineering Works**" was designed, built, and operated by chemical engineers. **Equipment** never before conceived of; had to be **designed**, **built**, and **tested** using great **haste**.**Remote processing** and **control** of the plutonium pile was a must. Even **remote repair** was put into place to fix equipment that broke down after becoming radioactive. The Hanford plant was **big**, **complex**, and dealt with the **most dangerous materials** on the planet. It demonstrates what is often expected of chemical engineers. **Seeminglyimpossible problems** must be **solved quickly**, **correctly**,**economically**, and **safely**, using knowledge of both**chemistry and engineering**.

Post-War Growth

During World War II, American chemical engineers where called upon to build and operate many new facilities; some never having been before conceived (see Atomic Bomb above). After the war, **Germany's massive chemical industry lay in ruins** while the **Americans** were still operating at full production. Never the less, the United States Government **still feared** the **German chemical complex**. They therefore **dismantled** Hitler's enormous **I.G.Farben**and out of it three new companies where **created**; **BASF**,**Bayer**, and **Hoechst**.

With foreign competition almost non-existent, the **U.S. chemical industry** continued its **meteoric rise**; with**petroleum** continuing to be the **foundation** of the industry. From **fuels** and **plastics** to **fine chemicals**, petroleum was where the action was. Some have even argued that World War I & II were fought exclusively for the control of petroleum resources (see "The Prize" by Daniel Yergin). The**success** of the **petroleum industry** has helped the chemical engineering profession greatly, and is one of the reasons **today's wages are so high** (see WAGES).

With America firmly leading the world in chemical technology,**chemical engineering education** began to **change**. Suddenly, the best way to discover the latest events in chemical

technology was **not to pick up a German technical journal**, but **instead** to **make those discoveries yourself**. **Chemical engineering** was**becoming** more **focused** on **science** than on engineering tradition.

Two universities did much to encourage these events. At the**University of Minnesota**, **Amundson and Aris** began emphasizing the importance of **mathematical modeling**(using dimensionless quantities) in **reactor design**. And at the **University of Wisconsin, Bird, Stewart, & Lightfoot**presented a **unified mathematical description** of **mass, momentum, and energy transfer** in their now famous text, "**Transport Phenomena**." These events were **far removed** from the **early days** of the profession, when the possibility of **eliminating most mathematical courses**was strongly **considered**.

Today's Multi-Discipline

For the last **twenty years**, large **changes** have occurred in the American chemical industry. Most of the **major engineering obstacles** found in petroleum processing have been **overcome**, and **petroleum** is becoming a **commodity industry**. This means that **employment opportunities** for engineers in the petroleum industry are becoming **few and far between**.

Also, **foreign competition** has again **picked up**. Today the**three largest chemical companies** in the world are **BASF**,**Bayer**, and **Hoechst** (perhaps our government's fears where justified, see Post War Growth above; also it is important to point out that **Japan** does **not** represent a **major chemical threat**, instead the competition comes from Europe). While**America's chemical industry** can still compete, **growth**has **slowed** immensely. In short, the **unprecedented economic success** that **followed World War II** is **coming to a close** and economic realities are catching up with us (at least in the chemical industry).

However, the strong **scientific**, **mathematical**, and**technical background** found in chemical engineering education is **allowing** the **profession** to **enter new fields**that often lay in the white space between disciplines. The largest growth in employment is occurring in up-and-coming fields that show tremendous potential. **Biotechnology**,**electronics**, **food processing**. **pharmaceuticals**,**environmental clean-up**, and **biomedical implants** all offer possibilities for chemical engineers. The educational emphasis of the last twenty years has helped to realize these opportunities. *Once again, chemical engineering education has responded to, and influenced, the industrial realities of the profession*.

The Physics and The Chemical Law List

The Laws List

Laws, rules, principles, effects, paradoxes, limits, constants, experiments, & thought-experiments in physics.

Introduction. The laws list is a list of various laws, rules, principles, and other related topics in physics and astronomy.

This list is not intended to be complete.

History. The laws list originally started out strictly as a list of laws. Then, because of their similarity, I began adding rules to the list (after all, in physics, there is generally no difference between a law and a rule). Over time I added more and more similarsubjects. Now, the list is more of a minidictionary of physics andastronomy terms, rather than strictly a list of laws, rules, and so forth; however, for historical reasons I still refer to it as the lawslist, even though it is something of a misnomer.

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The laws list: V

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The laws list: Y

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The laws list: Z

CHEMICAL PROCESS CALCULATIONS : UNIT MEASURES

Mathematical Notation for Orders of Magnitude

Mathematical Power	Name
10^{18} or 1,000,000,000,000,000,000	one quintillion
10^{15} or 1,000,000,000,000,000	one quadrillion
10^{12} or 1,000,000,000,000	one trillion
10^{9} or 1,000,000,000	one billion
10^{6} or 1,000,000	one million
10^{3} or 1,000	one thousand
10^{2} or 100	one hundred
10^{1} or 10	ten
10^{0} or 1	one
10^{-1} or 0.1	one-tenth
10^{-2} or 0.01	one-hundredth

10^{-3} or 0.001	one-thousandth
10^{-6} or 0.000 001	one-millionth
10^{-9} or 0.000 000 001	one-billionth
10^{-12} or 0.000 000 000 001	one-trillionth
10^{-15} or 0.000 000 000 000 001	one-quadrillionth
10^{-18} or 0.000 000 000 000 000 001	one-quintillionth

Metric Prefixes

Conversions from a multiple or submultiple to the basicunits of meters, liters, or grams can be done using the table. For example, to convert from kilometers to meters, multiply by 1,000 (9.26 kilometers equals 9,260 meters) or to convert from meters to kilometers, multiply by 0.001 (9,260 meters equals 9.26 kilometers).

Prefix Symbol Length, weight,

or capacity Area Volume

exa E 10^18 10^36 10^54

peta P 10^15 10^30 10^45

tera T 10^12 10^24 10^36

giga G 10^9 10^18 10^27

mega M 10^6 10^12 10^18

hectokilo hk 10^5 10^10 10^15

myria ma 10^4 10^8 10^12

kilo k 10^3 10^6 10^9

hecto h 10^2 10^4 10^6

basic unit - 1 meter, 1 meter^2 1 meter^3

1 gram,

1 liter

deci d 10-^1 10-^2 10-^3

centi c 10-^2 10-^4 10-^6

milli m 10-^3 10-^6 10-^9

decimilli dm 10-^4 10-^8 10-^12

centimilli cm 10-^5 10-^10 10-^15

micro u 10-^6 10-^12 10-^18

nano n 10-^9 10-^18 10-^27

pico p 10-^12 10-^24 10-^36

femto f 10-^15 10-^30 10-^45

atto a 10-^18 10-^36 10-^54

Conversion of Units

Instructions
euro currencies!

Symbol US-Name ------ ------- A amp (ampere) C coul (coulomb) dyn dyne erg erg F farad

G gauss g gm (gram) H henry Hz hz (hertz) J joule K degC (kelvin) kg kg (kilogram) l liter m m (meter) MHz mhz (megahertz) ml ml (milliliter) mol Mx maxwell N nt (newton) Oe oe (oersted) P poise Pa pascal s s (sec, second) St stoke T tesla V volt W watt Wb weber Ohm ohm

Constantsa0 Bohr radius (bohrradius) alpha reciprocal fine structure constant amu atomic mass unit au astronomical unit c speed of light in vacuum e elementary charge epsilon permittivity of vacuum (permittivity) faraday Faradayconstant force acceleration of gravity
gammae electrongyromagnetic ratio gammap proton gyromagnetic ratio (in water)
ge electron Lande factor (g value) gH proton Lande factor grav acceleration of gravity (same as force) Grav gravitational constant (gravity) h Planck constant(planckconstant) hartree atomic energy unit hbar h/2 pi (hquer) k Boltzmann constant (boltzmannconstant) lambdac Compton wavelength (comptonwavelength) me electron rest mass (electronmass) mn neutron rest mass (neutronmass) mp proton rest mass (protonmass) mole equal to

Avogadro'snumber (pure number!) Mol same as mole mu permeability of vacuum (permeability) muB Bohr magneton (mub, bohrmagneton) mun nuclear magneton (muN, nuclearmagneton) NA Avogadro's number (unit /mol) nueelectron Larmor frequency factor nup proton Larmorfrequency factor pi 3.14159... (Ludolf's number) R gasconstant Vmol molar volume

The script makes use of the Unix program **units**. For further details, see the man page of units

About Temperature

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What is Temperature?

In a qualitative manner, we can describe the temperature of an object as that which determines the sensation of warmth or coldness felt from contact with it.

It is easy to demonstrate that when two objectsof the same material are placed together (physicists say when they are put in thermal contact), the object with the higher temperature cools while the cooler object becomes warmer until a point is reached after which no more change occurs, and to our senses, they feel the same. When the thermal changes have stopped, we say that the two objects (physicists define them more rigorously as systems) are in*thermal equilibrium* . We can then define the temperature of the system by saying that the temperature is that quantity which is the same for both systems when they are in thermal equilibrium.

If we experiment further with more than two systems, we find that many systems can be brought into thermal equilibrium with each other; thermal equilibrium does not depend on the kind of object used. Put more precisely,

if two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other,

and they all have the same temperature regardless of the kind of systems they are.

The statement in italics, called the *zeroth law of thermodynamics* may be restated as follows:

If three or more systems are in thermal contact with each other and all in equilibrium together, then any two taken separately are in equilibrium with one another. (quote from T. J. Quinn's monograph *Temperature*)

Now one of the three systems could be an instrument calibrated to measure the temperature - i.e. a thermometer. When a calibrated thermometer is put in thermal contact with a system and reaches thermal equilibrium, we then have a quantitative measure of the temperature of the system. For example, a mercury-in-glass clinical thermometer is put under the tongue of a patient and allowed to reach thermal equilibrium in the patient's mouth - we then see by how much the silvery mercury has expanded in the stem and read the scale of the thermometer to find the patient's temperature.

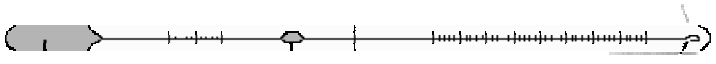
What is a Thermometer?

A thermometer is an instrument that measures the temperature of a system in a quantitative way. The easiest way to do this is to find a substance having a property that changes in a regular way with its temperature. The most direct 'regular' way is a linear one:

$t(x) = ax + b,$

where t is the temperature of the substance and changes as the property x of the substance changes. The constants a and b depend on the substance used and may be evaluated by specifying two temperature points on the scale, such as 32° for the freezing point of water and 212° for its boiling point.

For example, the element mercury is liquid in the temperature range of -38.9° C to 356.7° C (we'll discuss the Celsius ° C scale later). As a liquid, mercury expands as it gets warmer, its expansion rate is linear and can be accurately calibrated.



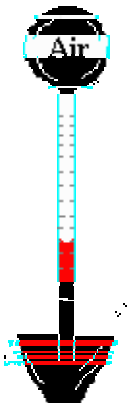
The mercury-in-glass thermometer illustrated in the above figure contains a bulb filled with mercury that is allowed to expand into a capillary. Its rate of expansion is calibrated on the glass scale.

The Development of Thermometers and Temperature Scales

The historical highlights in the development of thermometers and their scales given here are based on "Temperature" by T. J. Quinn and "Heat" by James M. Cork.

One of the first attempts to make a standard temperature scale occurred about AD 170, when Galen, in his medical writings, proposed a standard "neutral" temperature made up of equal quantities of boiling water and ice; on either side of this temperature were four degrees of heat and four degrees of cold, respectively.

The earliest devices used to measure the temperature were called thermoscopes.



They consisted of a glass bulb having a long tube extending downward into a container of colored water, although Galileo in 1610 is supposed to have used wine. Some of the air in the bulb was expelled before placing it in the liquid, causing the liquid to rise into the tube. As the remaining air in the bulb was heated or cooled, the level of the liquid in the tube would vary reflecting the change in the air temperature. An engraved scale on the tube allowed for a quantitative measure of the fluctuations.

The air in the bulb is referred to as the *thermometric medium*, i.e. the medium whose property changes with temperature.

In 1641, the first sealed thermometer that used liquid rather than air as the thermometric medium was developed for Ferdinand II, Grand Duke of Tuscany. His thermometer used a sealed alcohol-in-glass device, with 50 "degree" marks on its stem but no "fixed point" was used to zero the scale. These were referred to as "spirit" thermometers.

Robert Hook, Curator of the Royal Society, in 1664 used a red dye in the alcohol . His scale, for which every degree represented an equal increment of volume equivalent to about 1/500 part of the volume of the thermometer liquid, needed only one fixed point. He selected the freezing point of water. By scaling it in this way, Hook showed that a standard scale could be established for thermometers of a variety of sizes. Hook's original thermometer became known as the standard of Gresham College and was used by the Royal Society until 1709. (The first intelligible meteorological records used this scale).

In 1702, the astronomer Ole Roemer of Copenhagen based his scale upon **two** fixed points: snow (or crushed ice) and the boiling point of water, and he recorded the daily temperatures at Copenhagen in 1708- 1709 with this thermometer.

It was in 1724 that Gabriel Fahrenheit, an instrument maker of Däanzig and Amsterdam, used mercury as the thermometric liquid. Mercury's thermal expansion is large and fairly uniform, it does not adhere to the glass, and it remains a liquid over a wide range of temperatures. Its silvery appearance makes it easy to read.

Fahrenheit described how he calibrated the scale of his mercury thermometer:

"placing the thermometer in a mixture of sal ammoniac or sea salt, ice, and water a point on the scale will be found which is denoted as zero. A second point is obtained if the same mixture is used without salt. Denote this position as 30. A third point, designated as 96, is obtained if the thermometer is placed in the mouth so as to acquire the heat of a healthy man." (D. G. Fahrenheit,*Phil. Trans. (London)* 33, 78, 1724)

On this scale, Fahrenheit measured the boiling point of water to be 212. Later he adjusted the freezing point of water to 32 so that the interval between the boiling and freezing points of water could be represented by the more rational number 180. Temperatures measured on this scale are designated as**degrees Fahrenheit (° F)**.

In 1745, Carolus Linnaeus of Upsula, Sweden, described a scale in which the freezing point of water was zero, and the boiling point 100, making it a *centigrade* (one hundred steps) scale. Anders Celsius (1701-1744) used the reverse scale in which 100 represented the freezing point and zero the boiling point of water, still, of course, with 100 degrees between the two defining points.

In 1948 use of the Centigrade scale was dropped in favor of a new scale using **degrees Celsius (° C)**. The Celsius scale is defined by the following two items that will be discussed later in this essay:

(i) The triple point of water is defined to be 0.01° C.
(ii) A degree Celsius equals the same temperature change as a degree on the ideal-gas scale.

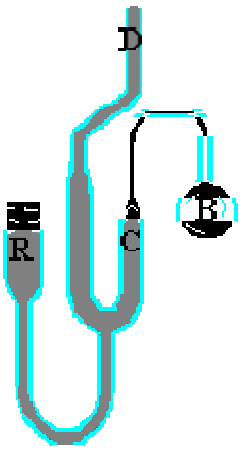
On the Celsius scale the boiling point of water at standard atmospheric pressure is 99.975 C in contrast to the 100 degrees defined by the Centigrade scale.

To convert from Celsius to Fahrenheit: multiply by 1.8 and add 32.

° F = 1.8° C + 32
° K = ° C + 273.

(Or, you can get someone else to do it for you!)

In 1780, J. A. C. Charles, a French physician, showed that for the same increase in temperature, all gases exhibited the same increase in volume. Because the expansion coefficient of gases is so very nearly the same, it is possible to establish a temperature scale based on a single fixed point rather than the two fixed- point scales, such as the Fahrenheit and Celsius scales. This brings us back to a thermometer that uses a gas as the thermometric medium.



In a constant volume gas thermometer a large bulb B of gas, hydrogen for example, under a set pressure connects with a mercury-filled "manometer" by means of a tube of very small volume. (The Bulb B is the temperature-sensing portion and should contain almost all of the hydrogen). The level of mercury at C may be adjusted by raising or lowering the mercury reservoir R. The pressure of the hydrogen gas, which is the "x" variable in the linear relation with temperature, is the difference between the levels D and C plus the pressure above D.

P. Chappuis in 1887 conducted extensive studies of gas thermometers with constant pressure or with constant volume using hydrogen, nitrogen, and carbon dioxide as the thermometric medium. Based on his results, the Comité International des Poids et Mesures adopted the constant-volume hydrogen scale based on fixed points at the ice point (0° C) and the steam point (100° C) as the practical scale for international meteorology.

Experiments with gas thermometers have shown that there is very little difference in the temperature scale for different gases. Thus, it is possible to set up a temperature scale that is independent of the thermometric medium if it is a gas at low pressure. In this case, all gases behave like an "Ideal Gas" and have a very simple relation between their pressure, volume, and temperature:

$pV = (\text{constant})T$.

This temperature is called the *thermodynamic temperature*and is now accepted as the fundamental measure of temperature. Note that there is a naturally-defined zero on this scale - it is the point at which the pressure of an ideal gas is zero, making the temperature also zero. We

will continue a discussion of "absolute zero" in a later section. With this as one point on the scale, only one other fixed point need be defined. In 1933, the International Committee of Weights and Measures adopted this fixed point as the triple point of water , the temperature at which water, ice, and water vapor coexist in equilibrium); its value is set as 273.16. The unit of temperature on this scale is called the kelvin, after Lord Kelvin (William Thompson), 1824-1907, and its symbol is K (no degree symbol used).

To convert from Celsius to Kelvin, add 273.

K = ° C + 273.

Thermodynamic temperature is the fundamental temperature; its unit is the kelvin which is defined as the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

Sir William Siemens, in 1871, proposed a thermometer whose thermometric medium is a metallic conductor whose resistance changes with temperature. The element platinum does not oxidize at high temperatures and has a relatively uniform change in resistance with temperature over a large range. The *Platinum Resistance Thermometer* is now widely used as a thermoelectric thermometer and covers the temperature range from about -260° C to 1235° C.

Several temperatures were adopted as Primary reference points so as to define the International Practical Temperature Scale of 1968. The International Temperature Scale of 1990 was adopted by the International Committee of Weights and Measures at its meeting in 1989. Between 0.65K and 5.0K, the temperature is defined in terms of the vapor pressure - temperature relations of the isotopes of helium. Between 3.0K and the triple point of neon (24.5561K) the temperature is defined by means of a helium gas thermometer. Between the triple point of hydrogen (13.8033K) and the freezing point of silver (961.78°K) the temperature is defined by means of platinum resistance thermometers. Above the freezing point of silver the temperature is defined in terms of the Planck radiation law.

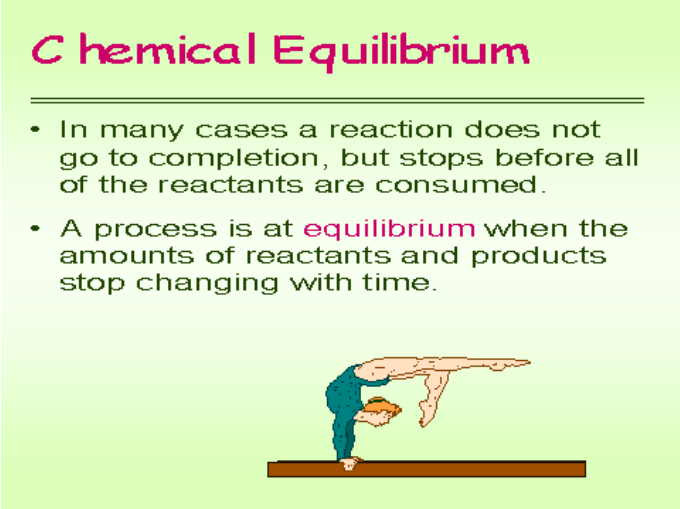
T. J. Seebeck, in 1826, discovered that when wires of different metals are fused at one end and heated, a current flows from one to the other. The electromotive force generated can be quantitatively related to the temperature and hence, the system can be used as a thermometer - known as a thermocouple. The thermocouple is used in industry and many different metals are used - platinum and platinum/rhodium, nickel-chromium and nickel-aluminum, for example. The National Institute of Standards and Technology (NIST) maintains databases for standardizing thermometers.

For the measurement of very low temperatures, the magnetic susceptibility of a paramagnetic substance is used as the thermometric physical quantity. For some substances, the magnetic susceptibility varies inversely as the temperature. Crystals such as cerrous magnesium nitrate and chromic potassium alum have been used to measure temperatures down to 0.05 K; these crystals are calibrated in the liquid helium range. This diagram and the last illustration in this text were

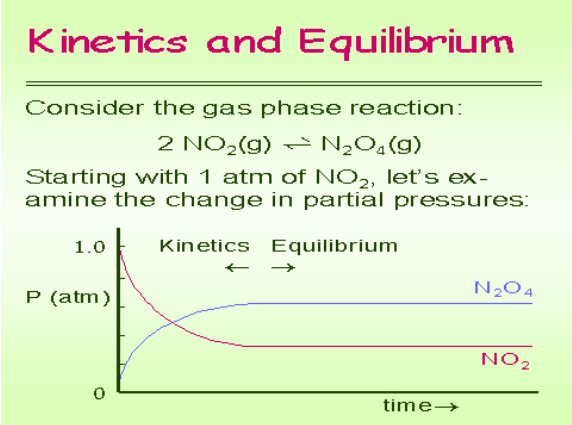
taken from the Low Temperature Laboratory, Helsinki University of Technology's picture archive. For these very low, and even lower, temperatures, the thermometer is also the mechanism for cooling. Several low-temperature laboratories conduct interesting applied and theoretical research on how to reach the lowest possible temperatures and how work at these temperatures may find application.

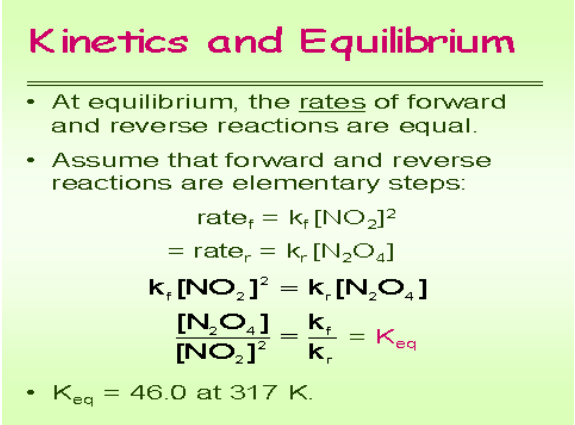
Chemical Reaction Engineering

Chemical Equilirium



Kinetics and Equilibrium





The Equilibrium Expression

The Equilibrium Expression

For the general reaction:

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

The equilibrium expression is

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K_c is the equilibrium constant. The equilibrium constant depends only on temperature.

The Equilibrium Expression

What is the equilibrium expression for the reaction:

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \quad ?$$

$$K_c = \frac{[N_2]^1[H_2]^3}{[NH_3]^2}$$

Equilibrium can be reached either by mixing N_2 and H_2, or by dissociating pure NH_3.

Gas Phase Reactions

Gas Phase Reactions

For reactions in the gas phase, the equilibrium expression can be expressed in terms of partial pressures.

For the reaction:

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$$

The equilibrium expression is:

$$K_p = \frac{P^2_{NOCl}}{P^2_{NO}\,P_{Cl_2}}$$

K_p is the equilibrium constant in pressure units.

The Relationship Between Kp and Kc

The Relationship Between K_p and K_c.

K_C for gas phase reactions can be found using the ideal gas law:

$$A(g) + 3\,B(g) \rightleftharpoons 2\,C(g)$$

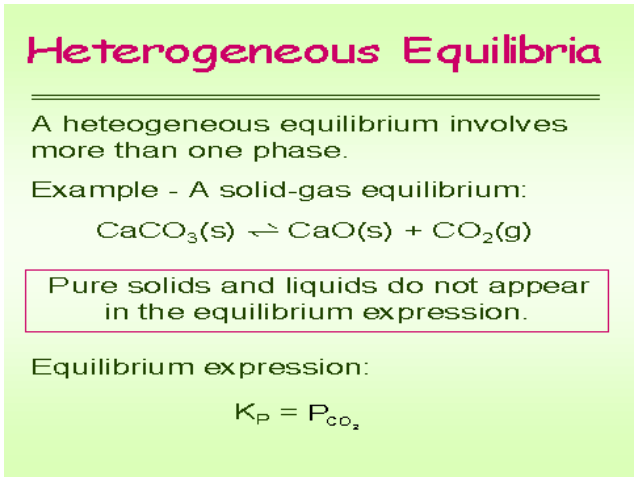
$$K_P = \frac{P_C^2}{P_A\,P_B^3} = \frac{\left(\frac{n_C RT}{V}\right)^2}{\left(\frac{n_A RT}{V}\right)\left(\frac{n_B RT}{V}\right)^3}$$

$$K_P = \frac{[C]^2}{[A][B]^3}(RT)^{-2} = K_c(RT)^{-2}$$

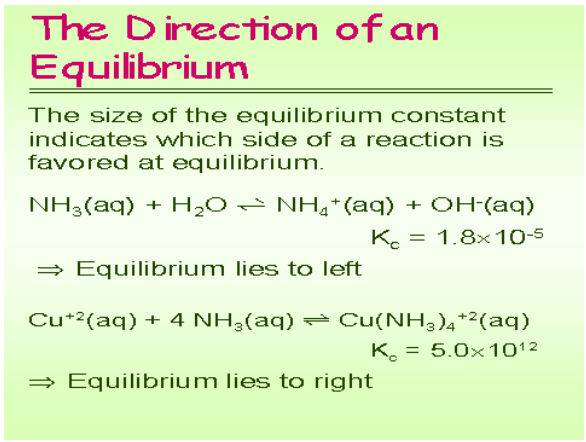
In general: $K_P = K_c(RT)^{\Delta n}$

Δn = mols products - mols reactants

Heterogeneous Equilibria



The Direction of Equilibrium



Solid Fluid Operations

- Engineering Aspects in Solid Liquid Separation
- Filtration and Separation Spreadsheet files
- Reactive Distillation
- Tower Sizing and Pricing
- Distillation Introduction
- Making Ball Mill
- Freely Moving Particles

Engineering Aspects in Solid Liquid Separation

Solid-Liquid Separation is a major unit operation that exists in almost every flowscheme related to the chemical process industries, ore beneficiation, pharmaceutics, food or water and waste treatment. The separation techniques are very diverse and the objective of this site is to provide a platform for plant and design engineers, research personnel and students to discuss practices, experiences and new developments in this fascinating unit operation.

The site is still under construction and so far the following sections have been completed:

- Vacuum Filters - the entire section.
- Pressure Filters - the entire section.
- Thickeners - the section on Conventional Thickeners and High-Rate Thickeners

Sections that will be soon added:

- Lamella - to the Thickeners section
- Clarifiers - the sections on Conventional and Sludge Blanket Clarifiers

The site, when completed, will review the following topics:

- Filtration by vacuum and pressure filters.
- Polishing by vacuum precoat filters and pressure filters.
- Centrifugation by filtering and sedimenting centrifuges.
- Sedimentation by conventional, storage and high-rate thickeners .
- Clarification by conventional, solids-contact and sludge-blanket clarifiers.
- Ancillary equipment, vacuum pumps, filtrate pumps, vacuum receivers, moisture traps

This site does not cover separation methods such as screening, hydrocycloning, froth flotation and dissolved-air flotation due to my limited experience in these applications.

Other related subjects that will be discussed are:

- Coagulation and flocculation by bridging polymers.
- Moisture reduction by wetting agents.
- Particle analysis and its influence on performance.
- Defining a Relative Filtration Index during the research phase.
- Establishing diminishing returns on wash efficiencies and drying.
- Filtering medium and its selection.
- Evaluating long-term effects on separation rates.

Filtration and Separation Spreadsheet files

Many of the spreadsheet routines have been followed by a new site now, providing inter-active user data input and real time filtration and sedimentation modelling/simulation. An expert system for filter selection is also available. Here is the link to take you to: Filtration-and-Separation.com for these utilities.

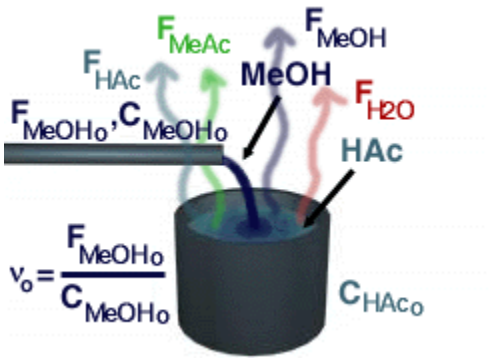
The original spreadsheets were written before Windows'95 and used Boorland - later Corel - Quattro Pro v5. The original files are still available below but I think most will wish to download the newer Excel'97 versions. Thus this page is structured as follows: a pdf file that describes some uses for the files, the Excel files in zip archive format and then the original Quattro Pro files. All the files have been revised for compatibility with the forthcoming second edition of the bookSolid-Liquid Filtration and Separation Technology, VCH, by Albert Rushton, Tony Ward and myself. The book will be out in late 1999 and full details of the basis for the simulations and how to use them are in it.

Regarding computer viruses, you may like to know that NONE of these files have macros in them.

fs.pdf (527k) This is a paper giving details of the files in Acrobat format, it's big but contains lots of useful details onwhat to look for.

Reactive Distillation

Introduction



$$CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O$$

Acetic Acid Methanol Methyl Acetate Water

Reactive distillation is used with **reversible**, **liquid phase** reactions. Suppose a reversible reaction had the following chemical equation :

$$A + B \rightleftharpoons C + D$$

For many revesible reactions the equilibrium point lies far tothe left and little product is formed :

$$A + B \rightleftharpoons C + D$$

However, if one or more of the products are removed more of the product will be formed because of Le Chatlier's Principle :

$$A + B \rightleftharpoons C + D\uparrow$$

Removing one or more of the products is one of the principles behind reactive distillation. The reaction mixture is heated and the product(s) are boiled off. However, caution must be taken that the reactants won't boil off before the products.

For example, Reactive Distillation can be used in removing acetic acid from water. Acetic acid is the byproduct of several reactions and is very usefull in its own right. Derivatives of acetic acid are used in foods, pharmaceuticals, explosives, medicinals and solvents. It is also found in many homes in the form of vinegar. However, it is considered a polutant in waste water from a reaction and must be removed.

Tower Sizing and Pricing

The program that I have posted on this page can be used to perform preliminay size and cost estimates for distillation columns with internal trays. It is in Microsoft Excelformat (version 5.0 or greater) and runs as an Excel Add-In. The program assumes cooling water (water entering at 30^0C and leaving no higher than 45^0C) is used in the condenser. LPS (Low Pressure Steam) is assumed to be at 5 barg and 160^0C, MPS (Medium Pressure Steam) at 10 barg and 184^0C, and HPS (High Pressure Steam) at 41 barg and 254^0C. Here are some other details of the this EXCEL ADD-IN:

- The condenser is priced as a Fixed Head Exchanger
- The reboiler is priced as a Floating Head Exchanger
- Minimal inputs are required for the column sizing and pricing
- Returned values include the cost of the vessel, trays, reboiler, condenser, steam, cooling water, and a local Net Present Value (over 10 years at an interest rate of 10%) for the column operation. This value can beused for optimization
- Utility prices used are: LPS $3.17/GJ, MPS $3.66/GJ, HPS $5.09/GJ, and CW $0.16/GJ
- The equipment is prices using correlations developed by G. D. Ulrich in *A Guide to Chemical EngineeringProcess Design and Economics*, Wiley, New York 1984. These correlations have also been reprinted in*Analysis, Synthesis, and Design of Chemical Processes*by Richard Turton, Richard Baile, Wallace Whiting, and Joseph Shaeiwitz (Prentice Hall, 1998). These correlations are well developed and provide a good degree of accuracy for a preliminary design.
- Length and diameter of column is also estimated

Transfer Function

What can you learn from the transfer function?

Knowing the transfer function of a system (controlled or uncontrolled) allows you to infer many things about its
performance. The most important things you can learn from the transfer function, H (s) are

summarized here:
1. Stability Start with the output of a continuous system in thecomplex frequency (-s) domain:
Notice that the inverse laplace transform o (t) the output as a time- function will be a sum of exponentials with each term looking like
This says that regardless of the mature of the input if the system has any poles that lie in the right half of the complexplane the output will contain terms that grow without limit
Therefore, any continuous system with poles in the right half of the complex plane is unstable, also in order to determine if a system is unstable, all you need to do is to find its poles, provided you can find the system poles, any other alternative method of determining stability is
unnecessary the GSim Compute poles. Vi will compute the poles of any transfer function for which the a – coefficients are known.
2. Relative importance of poles: the dominant- pole approximation
The residue-pole form of 0(s), above, lets you rank the relative contribution of each pole two different ways:
a) reative magnitude, determined by the relative magnitude of each residue, a
b) decay rate determined by the pole's horizontal location in the complex plane
outputs from poles located far to the left in the complex plane decay so quickly that they are of lesser importance
relative to outputs arising from poles further to the right in the complex plane.
it many cases you can approximate the transfer function of a high- order system with a lower-order one containing only the
dominant poles (those located closest to the imaginary axis)
3 steady- state errors
A control system designer who is not too demanding might be happy with a control system that finally produces an output exactly as commanded by the control signal "if you wait long enough " this crude specifications is usually only a starting points but is you usually part of the list of specs the designer must meet.
If we define "error" as the difference between command and actual system output.
Then its LaPlace transform is

the final value theorem for laplace transforms says that For any function of time, e(t) clearly, e depends on r(t) so let's consider some special cases of practical interest: a) steady- state error for a step a step function input, R(s) =1/s:Zero steady- state error in this case means that, given enough time, the system should finally track a command signal exactly after the command signal changes discontinuously to a new constant level . in this case. for zero steady-state error limit should be unity. For a controlled system with unity feedback and cascade compensation, C(s). only ,I .e F (s) =1 using the transfer function, This result is important for the design guidance it provides: since in principle you can design C(s) however you wish , you guarantee zero steady-state error by putting a pole in C(s) at –o such as Where F(s) is any other rational polynomial

function of s classical control texts call this a type 1system since 1/s is the laplacetransform corresponding to integration you can think of this condition as a reqyurement for integrating the error signal e(t). if the error is

$$e_{ss} = \lim_{s \to 0} \frac{1}{s}[1 - H(s)]$$

Where F(s) is any other rationalpolynomial function of s classical control texts call this a type 1system since 1/s is the laplace transform corresponding tointegration you can think of this condition as a reqyurement for integrating the error signal e(t).

Laplace transforms

Laplace transforms provide a method for representing and analyzing linear systems using algebraic methods. In systems that begin undeflected and at rest the laplace's can directly replace the d/dt operation in differential equations. It is a superset of the phasor representation in that it has both a complex part, for the steady state response, but also a real part representing the transient part. As with the otherrepresentations the laplace s is related to the rate of change in the system.
The basic definition of the laplace transform is shown in figure 17.2. the normal convention is to show the function of time with a lower case letter, while the same function in the s-domain is shown in upper case. Another useful observation is the transform starts at . examples of the application of thetransform are shown in figure 17.3 for a step function and in figure 17.4 for a first order derivative.

$$F(s) = \int_0^\infty f(t)e^{-st}dt$$

where,

$f(t)$ = the function in terms of time t

$F(s)$ = the function in terms of the Laplace s

Figure 17.2 The Laplace transform

Aside: Proof of the step function transform.

For f(t) = 5,

$$F(s) = \int_0^\infty f(t)e^{-st}dt = \int_0^\infty 5e^{-st}dt = -\frac{5}{s}e^{-st}\Big|_0^\infty = \left[-\frac{5}{s}e^{-s\infty}\right] - \left[-\frac{5e^{-s0}}{s}\right] = \frac{5}{s}$$

Figure 17.3 Proof of the step function transform

Figure 17.4 proof of the first order derivative transform

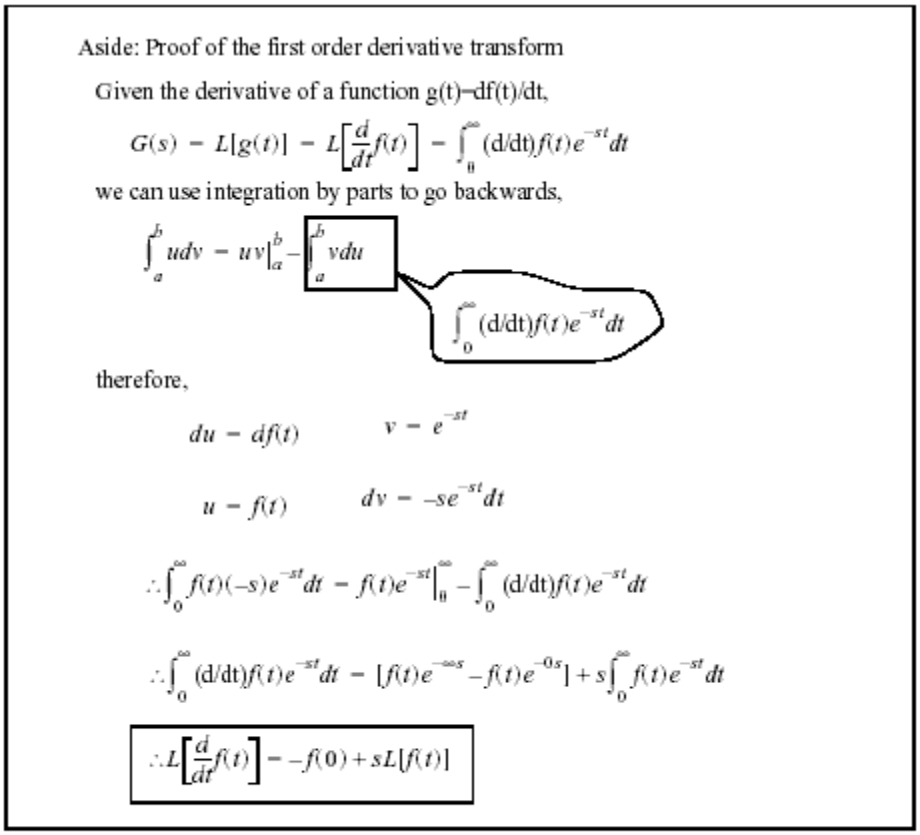


Figure 17.4 Proof of the first order derivative transform

The previous proofs were presented to establish the theoretical basis for this method, however tables of values will be presented in a later section for the most populartransforms.

Maths and System Identification

Solving of linear Equations using SVD

Solving of linear Equations using SVD

- Solving a linear equation
- Gauss elimination and SVD
- HowTo
- Some tricks for SVD

Problems in Linear Equations

- generally in solving **Ax=b** two error contributions possible:
  1. intrinsic errors in A and b
  2. numerical errors due to rounding
- Mathematical description and handling available

General Error Analysis

Matrix Norm necessary

- e.g.

$$\|A\|_2 = \max\{|\lambda|^{1/2},\ \lambda \text{ Eigenwert von } \bar{A}^T A\}$$

How does the final result (and its error) depend on the input value $\tilde{A} = A + \delta A$ and $\tilde{b} = b + \delta b$?

$$\frac{\|\delta x\|}{\|x\|} \leq \frac{\text{cond}(A)}{1 - \text{cond}(A)\|\delta A\|/\|A\|} \left\{ \frac{\|\delta b\|}{\|b\|} + \frac{\|\delta A\|}{\|A\|} \right\}$$

with

$$\text{cond}_2(A) := \|A\|_2 \|A^{-1}\|_2 = \frac{|\lambda_{\max}|}{|\lambda_{\min}|}$$

Eigenvalues of matrix

Example for Condition of Matrix

$$\begin{bmatrix} 1.2969 & 0.8648 \\ 0.2161 & 0.1441 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} = \begin{bmatrix} 0.8642 \\ 0.1440 \end{bmatrix}$$

Exact solution: **(2,-2)^T**

cond(A)=1.513x10^8

Change input values:

0.8642 → 0.86419999
0.1440 → 0.14400001

approximate solution: **(0.9911,-0.4870)^T**

NOT ACCEPTABLE!

Gauss Elimination

- Error due to rounding:

n=m=30 →10^{13}

$$\frac{\|\delta x\|_\infty}{\|x\|_\infty} \leq \frac{\mathrm{cond}(A)}{1 - \mathrm{cond}(A)\|\delta A\|_\infty / \|A\|_\infty} \{1.01 \cdot 2^{n-1}(n^3 + 2n^2)\,\mathrm{eps}\}$$

with eps = machine accuracy (double: ~10^{-16})

However, this is the worst case scenario!

Singular Value Decomposition

- here for (nxn) case, valid also for (nxm)
- Solution of linear equations numerically difficult for matrices with bad condition:
  - regular matrices in numeric approximation can be singular
  - **SVD** helps finding and dealing with the sigular values

How does SVD work

Definition of singular value decomposition:

$$U^T A V = \Sigma = diag(\sigma_1, \ldots, \sigma_p)$$

with *U* and *V* orthogonal matrices

singular values

$$\begin{pmatrix} \sigma_1 & & & \\ & \sigma_2 & & \\ & & \ddots & \\ & & & \sigma_n \end{pmatrix}$$

$$Av_i = \sigma_i u_i ,$$
$$A^T u_i = \sigma_i v_i ,$$

$$A^T A v_i = \sigma_i^2 v_i$$

σ_i are eigenvalues of A^TA

Solution

Solution of the Equation:

$$\bar{x} = \sum_{i=1}^{r} \frac{u_i^T b}{\sigma_i} v_i$$

numeric behaviour of SVD can be determined:

$$\|\delta A\|_2 \leq \text{eps} \|A\|_2$$

SVD after Golub and Reisch

Householder Matrix $P,Q=1-ww^T$
(numerically OK)

$$A = \begin{bmatrix} x & x & x & x \\ x & x & x & x \\ x & x & x & x \\ x & x & x & x \end{bmatrix} \rightarrow PA = A' = \begin{bmatrix} * & * & * & * \\ 0 & * & * & * \\ 0 & * & * & * \\ 0 & * & * & * \end{bmatrix}$$

$$A' = \begin{bmatrix} * & * & * & * \\ 0 & * & * & * \\ 0 & * & * & * \\ 0 & * & * & * \end{bmatrix} \rightarrow A'Q = A'' = \begin{bmatrix} x & * & 0 & 0 \\ 0 & * & * & * \\ 0 & * & * & * \\ 0 & * & * & * \end{bmatrix}$$

SVD after Golub and Reisch

- after a couple of iterations:

J_0 Bidiagonal form:

$$J_0 = \begin{bmatrix} q_1 & e_2 & 0 & 0 \\ 0 & q_2 & e_3 & * \\ 0 & 0 & q_3 & e_n \\ 0 & 0 & 0 & q_n \end{bmatrix}$$

with:

$$J_0 = P_n \ldots P_1 A Q_1 \ldots Q_{n-2}$$

Q and P Householder matirces

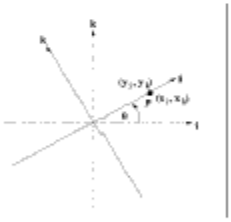
➢ A and J_0 have the same singular values

use iterative procedure to transform bidiagonal J_0 matrix to diagonal form

- apply 'Givens reflections' to bidiagonal Matrix:

$$\bar{J}_0 = S_{n-1,n} \ldots S_{23} S_{12} J_0 T_{12} T_{23} \ldots T_{n-1,n}$$

'Givens Reflection':



~cubic convergence expected

Arithmetic Expenses

- **Gauss (normal) solution**
  - $\frac{1}{2}mn^2+1/6n^3$
- **SVD Golub-Reinsch**
  - $2mn^2+4n^3$

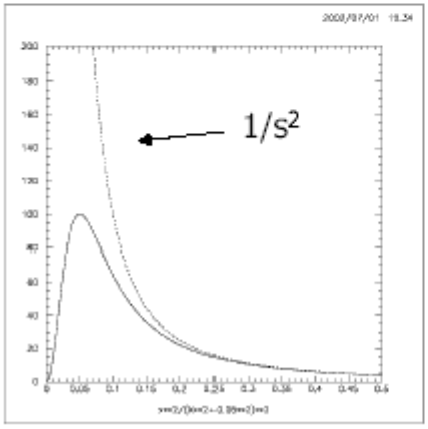
➢ **m=n :**

SVD is 9 times more expensive!

How to deal with Singularities

- singularities are determined with the SVD
- $1/\sigma_i$ is used for solution of linear equation
- relate $1/\sigma_i$ to machine accuracy and resolution τ
  - **usage of values $\sigma_i < \tau$ corrupts complet result!**
  - **careful handling necessary!**
- simple approach:
  - negelect all values in matrix with $\sigma_i < \tau$

Smooth cutoff

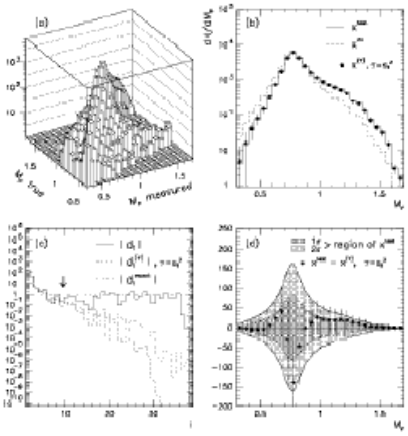


τ=0.05

- Regularisation of the singularities
- Replace the singular values with a function:

$$\frac{1}{s^2} \rightarrow \frac{s^2}{\left(s^2+t^2\right)^2}$$

Example



- Number-of-events response matrix

- $d_i \sim b_i/\Delta b_i$

  $d_i < 1 \rightarrow$ statistically insignificant

- Problem for alignment: determination of τ

Conclusion

- Numeric Solution of a regular linear equation can be distorted by singular behaviour
- SVD returns singular values
- Singular values can be handeld with smooth cut off
- Mathemaical well described procedure

Math Review Guide

MATHEMATIXL TOOLS
This contains additions and sections by Dr. Andrew Sterian.

we use math in almost every problem we solve . as a results of mathematics. But it is designed to be a quick reference guide to support the engineer required to usetechniques that may not have been used recently.

For those planning to write the first ABETF fundamentals of engineering exam, the following topics are commonly on the exam.

-Quadratic equation
-Straight line equations –slop and perpendicular
-Conics, circles, ellipses, etc.
-Matrices, determinants, ad joint, inverse, cofactors, multiplication
-Limits, L ‘Hospital’s rule, small angle approximation

-Integration of areas
-Complex numbers, polar from, conjugate, addition of polar forms
-Maxima, minima and inflection points
-First –order differential equation – linear, homogeneous, non-homogeneous second-order
-triangles, sine , cosine, etc.
-Integration- by parts and separation
-Solving equations using inverse matrices, cramer's rule, substitution
-Eigenvalues, eigenvectors
-dot and cross products, areas of parallelograms, angles and triple product
-Divergence and curl- solenoidal and conservative fields
-Centroids
-Integration of volumes
-integration using Laplace transforms
-probability- permutations and combinations
-mean, standard deviation, mode, etc.
-log properties
-Taylor series
-partial fractions
-basic coordinate transformations- Cartesian, cylindrical, spherical
-trig identities
-derivative- basic, natural log, small approx. chain rule. partial fractions

Constants and Other Stuff

A good place to start a short list of mathematical relationships is with Greek letters

lower case	upper case	name
α	A	alpha
β	B	beta
γ	Γ	gamma
δ	Δ	delta
ε	E	epsilon
ζ	Z	zeta
η	H	eta
θ	Θ	theta
ι	I	iota
κ	K	kappa
λ	Λ	lambda
μ	M	mu
ν	N	nu
ξ	Ξ	xi
o	O	omicror
π	Π	pi
ρ	P	rho
σ	Σ	sigma
τ	T	tau
υ	Y	upsilon
ϕ	Φ	phi
χ	X	chi
ψ	Ψ	psi
ω	Ω	omega

The constants listed are amount some of the main ones, other values can be derived through calculation using modern calculators or computers. The values are typically given with more than 15 places of accuracy so that they can be used for double precision calculations.

Stability, Controllability and Observability

Introduction

The chapter contains a discussion on some fundamental system properties. Stability from a geometric point of view, is related to the properties of system trajectories around anequilibrium point. Elementary Lyapunov techniques are employed to analyze and quantify the stability of a linear system . controllability is another grometric property of a system, describing the ability to “drive” the system states to arbitrary values through the control input. Its dual notion of absorbability describes the ability to infer the system states given output measurements in an interval. An elegant analysis of these structural properties is presented using sector space methods

Stability

Consider a differential equation $\dot{x} = f(x)$. An **equilibrium point** is a vector x_e such that $f(x_e) = 0$. In other words, if $x(t_0) = x_e$, then $x(t) = x_e$, for all $t \geq t_0$. Obviously, linear systems ($\dot{x} = Ax$) always have 0 as an equilibrium point. Geometric stability (in the sense of Lyapunov) is defined with respect to such equilibrium points: *"Given any $\epsilon > 0$, there exists a $\delta(\epsilon) > 0$ such that $\|x(t_0) - x_e\| < \delta \Rightarrow \|x(t) - x_e\| < \epsilon$, $\forall t \geq t_0$.* That is, the solution will stay close to the equilibrium for any initial condition "sufficiently close" it. Further, an equilibrium is said to be **asymptotically stable** if it is stable and $x(t) \rightarrow x_e$ as $t \rightarrow \infty$ for any initial condition sufficiently close to the equilibrium. In addition, if the convergence is exponential ($\|x(t) - x_e\| \leq K(x_0)e^{-a(t-t_0)}$, where $a > 0$ and $K(x_0)$ is a constant that depends on the initial conditions) the equilibrium is exponentially stable.

This notion of stability is different from the input-output (operator) stability where a system is L-stable if any input in L produces an output in L. here L is a sector space, eg bounded functions, energy functions etc .the input in describing performance specifications. On the other hand Lyapunovstability is suitable to describe convergence properties and provides a more appealing computational framework. While in the case of linear time invariant systems the two stabilitynotions are closely related, their differences become more pronounced (and technically involved) in the general nonlinear case.

The basic Lyapnov analysis begins with a positive definite function of the states, interpreted as the energy stored in the system, e.g. V(x) = xT px where P= PT>0. a sufficient condition for the asymptotic stability (stability) of the zeroequilibrium is that the derivative of thus function along the trajectories of the system (dV/dt =(oV0x)x) is negative definite (semi-definite). This can be viewed as a condition on the energy dissipation within the system. It is also a necessary condition in the sense that if an equilibrium is asymptotically stable, then there exists a Lyapunov function with the above properties . in general it is difficult to construct such a function. Nevertheless, in the case of linear systems the lyapunov functions are quadratic making their computation a straightforward exercise in matrix algebra.

To demonstrate the application of Lyapunov analysis, let us consider the system x= Ax and the function V = xT px thederivative of V along the trajectories of the system is computed as follows:

$$\dot{V} = \frac{\partial V}{\partial x}\frac{dx}{dt} = x^\top (A^\top P + PA)x$$

Next, suppose that the matrix $Q = -(A^\top P + PA)$ is positive definite.

Then, the following inequalities can be established:

$$\dot{V} \leq -\lambda_{min}(Q)\|x\|^2 \leq -\frac{\lambda_{min}(Q)}{\lambda_{max}(P)}V$$

Using the so-called comparison principle, it now follows that $V(t) \leq V(0)e^{-at}$ where $a = \frac{\lambda_{min}(Q)}{\lambda_{max}(P)}$. In turn, this implies that for any initial conditions, the system trajectories converge to the zero equilibrium exponentially fast. These derivations illustrate the essense of Lyapunov analysis for linear systems and are made precise by the following theorem:

4.2.1 Theorem: *Given a matrix $A \in \mathbf{R}^{n\times n}$ the following*
The eigenvalues of A have strictly negative real parts (A is **Hurwitz***).*

There exist positive constants K, a such that $\|e^{At}\| < Ke^{-at}$.
There exists some $Q = Q^\top > 0$ such that $A^\top P + PA = -Q$ has a unique solution for P and it is positive definite.

For any $Q = Q^\top > 0$, there exists a unique P such that $A^\top P + PA = -Q$ and this P is positive definite.

Notice that, for a Hurwitz matrix A not every positive definite P produces a positive definite Q : only the converse holds . the equation is referred to as Lyapunov . it is linear in P and can be solved as a system of linear equation has a unique solution (positive definite or not) iff any two eigenvalues of P satisfy .from a system theoretic , a more interesting property of Lyapunov equations is that for a Hurwitz A their solution has the form

$$P = \int_0^\infty e^{A^\top t} Q e^{At} dt$$

The last expression is extremely important for its analytical value. Among other applications, it allows an easy computation of controllability and observability Gramians as solutions of linear Lyapunov equations. These are an integral component of general model order reduction algorithms.

Lyapunov equations play an important role in several recent results on the design of control system via numerical optimization. For example consider the intermediate) problem where given a matrix A we would like to estimate the exponential rate of decay of the states to zero. This can be found as the real part of the eigenvalue of A closest to the jw-axis. However eigenvalues are nonlinear functions of the entries of A and are not suitable objectives for any (additional) optimization. Alternatively, we can ask to find the matrix Q that maximizes the ratio as previously shown this ratio provides an estimate of the rate of decay of the states can be shown that the optimal Q for this purpose is the identity. This problem can be cast as the optimization of a convex objective subject to convex constraints (linear matrix inequalities), and its solution can

be obtained with numerically efficient and reliable algorithms. The value estimate the jw-axis. However Of this approach lies in its ability to handle case where the matrix A is itself a convex function of other parameters. A simple example of that is to find a single Lyapunov function if it exists, that hasa negative definite derivative for two systems , i.e,

$$P = P^\top > 0: \quad A_1^\top P + P A_1 \leq -I \;\; ; \;\; A_2^\top P + P A_2 \leq -I$$

The existence of such a P would imply the stability of a system whose matrix A undergoes arbitrarily fast transitions between the values A1 and A2. this type of problems arises in the analysis and design of gain-scheduled control systems.

For linear systems it is straightforward to show that exponentialstability of the zero equilibrium (A being Hurwitz) also implies the input-output stability (in a BIBO or energy sense) of the system [A,B,X,D], for any B,C,D. the converse is not always true unless some additional conditions are imposed, e.g., controllability and observability. Furthermore, a somewhat similar statement is valid in a general nonlinear setting but with significantly more involved technical conditions.