# 6 IZDELAVA KEMIJSKEGA PRODUKTA

Izbrali smo najboljšo idejo (izjemoma dve) za produkt. Odločamo se, kako bo produkt izgledal in kako ga bomo izdelali.

Nov produkt je lahko osnovan na inovaciji (izumu). V tem primeru moramo razmisliti ali bomo poskušali sestavo, izdelavo in/ali delovanje produkta zaščititi s patentom ali ne. Druga možnost je, da se odločimo varovati poslovno skrivnost.

Pred izdelavo moramo pridobiti potrebne manjkajoče informacije, ki jih potrebujemo za izdelavo produkta (Prepričati se moramo, ali bo produkt deloval kot pričakujemo.) in/ali za patentno zaščito (Za prijavo patenta potrebujemo ogromno podatkov, poznati moramo vso dostopno literaturo iz vsebine, ki jo bo zajemal patent.). Manjkajoče informacije pridobimo s pomočjo skrbno izvedenih kemijskih in fizikalnih eksperimentov in tudi s prebiranjem vse dostopne literature.

Pred izdelavo moramo določiti končne specifikacije produkta. Pri tem uporabljamo raje pristop s prilagajanjem kot inovativen pristop.

Na osnovi kemijskih in inženirskih znanj razvijemo postopek za izdelavo produkta. Za izdelavo različnih produktov (specialne kemikalije, formulirani produkti, naprave...) uporabljamo različna znanja in postopke.

## 6.1 INTELEKTUALNA LASTNINA

Projektni team mora tudi v fazi izdelave kemijskega produkta razmišljati široko in ne samo o tehnologiji za nov produkt. Prepričati se mora, če so se razmere na trgu od začetka projekta spremenile (Ali ostajajo potrebe uporabnika iste? Ali izbrani produkt (še) odgovarja zahtevam trga? Ali trg še obstaja?), vprašati se mora kaj z intelektualno lastnino, ki se je razvila med delom na projektu.
Patentna zaščita intelektualne lastnine lahko konkurenci prepreči izdelavo produkta, ki je enak ali zelo podoben našemu, in drastično poveča naše prednosti, če bomo prvi na trgu. Če se odločimo, da bomo vložili patentno prijavo, potrebujemo pomoč pravnikov.

Primer Jerome Lemelson (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.):

> The case of Jerome Lemelson serves to indicate how important intellectual property rights can be in product commercialization. At his death in 1997, Lemelson had the distinction of having the third largest number of U.S. patents held by an individual (Edison and Land are one and two). He patented over 500 inventions, but commercialized none of them. Instead he made his money by licensing his inventions or often by suing companies that he felt had infringed his rights. For example, Lemelson claimed invention of the bar code long before it became a supermarket norm. He wanted payment for each bar code used on any product. Because there is a strong incentive for companies already marketing successful products to settle this type of action out of court, Lemelson's heirs have so far not found it necessary to reach the stage of a court verdict. At his death, Lemelson was believed to have an annual income of several hundred million dollars from his patent portfolio. A charitable foundation now exists with the sole purpose of defending and pursuing the Lemelson patents and disposing of the resulting income. Patents can make a lot of money; they can also make life very difficult if someone else holds them, even if the holder has no intention of going into competition with you.

**Patenti in poslovne skrivnosti**

Intelektualna lastnina se lahko razdeli na patente in poslovne skrivnosti.

Patent je sporazum med izumiteljem in državo. Če izumitelj prepriča državo, ki jo zastopa patentni urad, da je vsebina patentne prijave res izum (novost), patentni urad podeli izumitelju ekskluzivno pravico do izuma za določeno časovno obdobje. Izumitelj v patentu izum podrobno opiše – bralce patenta uči, kako produkt narediti in ga uporabljati. Pomeni, da s patentom razkrijemo sestavo, izdelavo in/ali delovanje produkta, vendar pa imamo ekskluzivno licenco za trženje produkta za določeno obdobje. To je zelo pomembno, ker lahko v tem obdobju zaslužimo več in zato hitro povrnemo stroške, ki so nastali pri razvoju produkta. Izumitelj si lahko obeta, da bo, če bo njegov produkt prvi na trgu, dobil tudi do 2/3 od prodaje produkta. Patent je lahko tudi mednaroden.

http://www.uil-sipo.si (17.10.2011):

> *"Patent je izključna pravica fizične ali pravne osebe za izum, ki je nov, na inventivni ravni in je industrijsko uporabljiv.*
> *Izum oziroma tehnična rešitev je nova, če ni obsežena s stanjem tehnike, se pravi, da ni bila pred datumom vložitve patentne prijave dostopna javnosti z ustnim ali pisnim opisom, z uporabo ali na katerikoli drug način.*
> *Izum je na inventivni ravni, če za strokovnjaka predmet izuma očitno ne izhaja iz stanja tehnike.*
> *Izum je industrijsko uporabljiv, če se predmet izuma lahko proizvede ali uporabi v katerikoli gospodarski dejavnosti, vključno s kmetijstvom.*
> *Odkritja, znanstvene teorije, matematične metode in druga pravila, načrti, metode in postopki za duhovno aktivnost se neposredno kot taki ne štejejo za izume in torej ne morejo biti predmet patentnega varstva. Patent tudi ne more biti podeljen za izume kirurškega ali diagnostičnega postopka ali postopka zdravljenja, ki se uporablja neposredno na živem človeškem ali živalskem telesu, razen izuma, ki se nanaša na izdelke, predvsem na snovi in zmesi, ki se uporabljajo pri takšnem postopku. S patentom se tudi ne da zavarovati izuma, katerega uporaba je v nasprotju z javnim redom ali moralo.*
>
> *Patent daje imetniku izključno pravico preprečiti tretjim, da bi brez njegovega soglasja izdelovali, uporabljali, ponujali v prodajo, prodajali ali v te namene uvažali predmete varovanega izuma. Imetnik patenta sam uveljavlja svojo pravico s tožbo pri pristojnem sodišču."*

Patent je pravna lastnina, zato se lahko kupi ali proda. Lahko kupimo licenco za patent (3−6 % od bruto prodaje).
Patent nam nudi pravno zaščito. Iz naslova patenta nam pripadajo pravice, ki pa jih je včasih težko zaščititi oziroma je to zelo drago.
Pogosto so patenti napisani zelo "na široko". Pogosto avtorji patenta kot možne surovine za produkt navajajo ogromno število kemikalij, med njimi tudi takšne, ki za konkreten produkt še niso bile testirane ali uporabljene. Namen prijavitelja patenta je, da z istim patentom zaščiti tudi intelektualno lastnino, ki jo še namerava osvojiti, ter da se zavaruje pred konkurenco. Po drugi strani, pa lahko prav na tak način konkurenci razkrije, s čem vse se še ukvarja ali s čem se ima namen ukvarjati.

V nasprotju s patentom je poslovna skrivnost informacija, ki je nujno potrebna za izdelavo in delovanje produkta, ki nima javnega značaja. Je kot PIN številka bančne kartice.
Poslovne skrivnosti niso pravna lastnina, zato so produkti, ki temeljijo na njih, vedno izpostavljeni visokemu tveganju.

Poslovno skrivnost lahko izgubimo, ko zaposleni menjajo službo. Našo poslovno skrivnost lahko (po naključju ali ne) odkrije konkurenca. Še huje je, če našo bivšo poslovno skrivnost konkurenca zaščiti s patentom in postane njena pravna last.
Včasih je izbira med patentom in ohranjanjem poslovne skrivnosti težka. Nekatere družbe se poslužujejo tretje rešitve. Intelektualne lastnine ne patentirajo in je tudi ne skrivajo kot poslovno skrivnost. Izum objavijo v strokovno in znanstveno nepomembni reviji ali v obliki posterja na kakšni konferenci z omejenim številom udeležencev. Možnost, da konkurenca vidi objavo mora biti zanemarljivo majhna. Dokumenti in potrdila o obstoju te objave morajo biti skrbno hranjeni. Vsebovati morajo natančne podatke o avtorstvu, času, kraju ter vsebini objave. V primeru, če bo kdaj konkurenca želela isto vsebino patentno zaščititi, ji bo to onemogočeno, ker vsebina po prvi objavi ni več novost oziroma izum.

**Zahteve za patent**

Kaj se lahko zaščiti s patentom in kako se izum dokumentira?

S patentom lahko zaščitimo novo in uporabno sestavo ali zgradbo snovi, izdelek, proces za izdelavo, design... Pomembno je, da je predmet patenta (produkt ali proces) koristen (uporaben) in da predstavlja resnično novost.

Navadno ni razloga, da bi patentirali produkt ali proces, ki ni koristen. Zato ustrezanje zahtevi po koristnosti v veliki večini primerov ni vprašljivo.

Da predmet patenta dejansko predstavlja novost, je potrebno ustrezno dokazati. Produkt ali proces ne smeta biti poznana ali uporabljena pred izumom, ki ga želimo zaščititi. Ne smeta biti predhodno zaščitena s patentom in/ali opisana v različnih objavah v pisni obliki (tudi če je avtor objave izumitelj).

Predmet patenta je novost takrat, ko se po naravi znatno razlikuje od predhodnih produktov in procesov. O neznatnem razlikovanju govorimo takrat, ko je zgolj manjša modifikacija obstoječega produkta (ali procesa) na osnovi povprečnih strokovnih znanj dovolj za izboljšavo. Takšna izboljšava ni prava novost in je ni mogoče zaščititi s patentom.

Pri prijavi patenta je zelo koristno, če imamo skrbno urejeno dokumentacijo o delu na razvoju produkta ali procesa, ki je privedel do izuma. Tovrstni dokumenti so pomembni dokazi, ki jih uveljavljamo pri patentni prijavi. Koristen dokument je laboratorijski dnevnik, v katerem so zapisani vsi opravljeni eksperimenti in dobljeni rezultati. Dnevnik mora biti opremljen z datumi in podpisi ter tedensko pregledan s strani odgovorne osebe ali presojevalca, ki ni hkrati izumitelj.

Primer (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**EXAMPLE 5.1–1 THE INVENTION OF THE WINDSURFER**

The windsurfer was patented by Hoyle Schweitzer in 1969. Schweitzer and an engineer, Jim Drake, set up a company, Windsurfing International Inc., and did much of the early development on windsurfing boards. For many years this company produced its own windsurfers and received license fees from other manufacturers. It was not until the late 1970s that windsurfing really took off, when the craze hit Europe; its greater popularity there is sometimes attributed the longer holidays common in Europe.

At this point, windsurfer manufacture became highly profitable, and large-scale manufacturers such as BIC, F2, and Mistral became heavily involved. These companies found it irksome to continue to have to pay a royalty to Windsurfing International every time they sold a board, and they began to search for ways to circumvent the patent. Eventually BIC discovered prior art, in the form of published material prior to the patent application date. In 1958 a British inventor, Paul Chilvers, was toying with something that looked a bit like a windsurfer; a picture was found in an obscure local paper. Also, in 1964, Newman Darby built a form of windsurfer (the Darby Sailboard) in Wilkes-Barre, PA. The Darby board used a universal joint to attach the mast to the board, one of the essential elements of the Schweitzer patent.

After a hotly contested legal battle, the patent was undermined by this prior art in both the U.S. and Europe. BIC no longer pays license fees (and nor does anyone else). We do not wish to suggest any ethical conclusion as to who deserves financial benefit. We would like this example to draw attention to the uncertainties and vicissitudes associated with the ownership of a patent.

## 6.2 ZAGOTAVLJANJE MANJKAJOČIH INFORMACIJ

V prejšnjem poglavju (Izbor) smo izbrali najbolj perspektivno idejo. Izbrali smo jo na osnovi informacij, ki so dostopne v literaturi, informacij, ki smo jih dobili v pogovorih z eksperti, s pomočjo inženirskih izračunov, ki so vključevali številne predpostavke in poenostavitve... Do tega trenutka smo poskušali minimizirati delo na vsakem koraku, eksperimentalnega dela smo opravili samo toliko, kot smo ga nujno potrebovali za primerjavo različnih idej med seboj. Zato informacije, ki jih imamo, niso kompletne in eksaktne.

Razvoj izdelave konkretnega produkta (na osnovi izbrane ideje s pomočjo procesa) zahteva veliko denarja, zato je bolje, če pred dejansko izdelavo natančno vemo, kako dobro bo naš produkt deloval ter kaj vse bo za njegovo izdelavo in delovanje potrebno. Potrebujemo več informacij, ki jih lahko pridobimo s pomočjo dodatnih raziskav in eksperimentalnega dela. Z eksperimentalnim delom moramo pridobiti manjkajoče potrebne podatke in znanje (ki niso dostopni v literaturi) ter potrditi vse (iz literature pridobljene) informacije, ki jih uporabljamo.

Razviti moramo funkcije lastnosti, procesne funkcije in uporabnostne funkcije.

### Reakcijske poti

Primer iskanja manjkajočih podatkov, ki so potrebni za načrtovanje specialnih kemikalij, je iskanje sintezne poti za sintezo aktivne molekule z znano kemijsko strukturo. Najti moramo sintezno pot, po kateri bomo lahko sintetizirali produkt in to v dovolj velikih količinah.

Eden izmed načinov je iskanje možnih reakcijskih korakov v smeri, ki je nasprotna od smeri sinteze: od produkta preko prekurzorjev do surovin. Na takšen način se lahko identificira več možnih sinteznih poti, vendar bodo le redke uporabne za proizvodni proces. Izberemo sintezno pot, ki je enostavna, varna, hitra, učinkovita, ekonomična...

Primeri (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

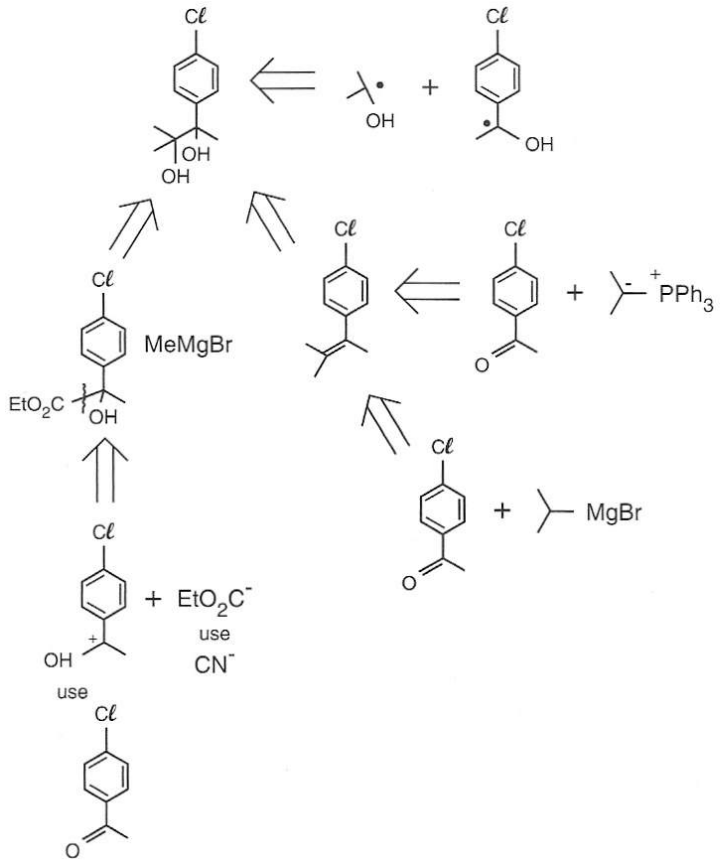



**Figure 5.2–1. Phenoglycodol Synthesis.** The drug, given in the upper left-hand corner of the figure, can be made by many routes. Three are sketched here. In these routes, each arrow indicates a possible "disconnection" step to simpler precursor molecules.

## EXAMPLE 5.2–1 SYNTHESIS OF THE TRANQUILIZER, PHENOGLYCODOL

The structure of this species is given in the upper left-hand corner of Figure 5.2–1. Suggest several routes by which it may be synthesized.

### SOLUTION

This is a fairly complex molecule and so many pathways are possible. The most obvious, also shown in Figure 5.2–1, use commercially available precursors. Which synthetic route we prefer will depend on other factors, such as cost, safety, and so on.

### EXAMPLE 5.2–2 STERICALLY HINDERED AMINES FOR $CO_2$ REMOVAL FROM GASES

Acid gas removal from gas streams (sweetening) is a very common process in the chemical and refining industries. For example, in a hydrogen plant, methane is converted by steam reforming to hydrogen and $CO_2$. The $CO_2$ must then be removed to leave a pure product. In an existing plant, this $CO_2$ removal is often the bottleneck for capacity expansion. For this reason, your company would like to improve $CO_2$ removal from gas streams. How can you do so?

SOLUTION

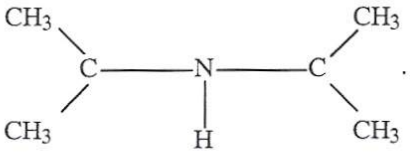
Conventionally, gas sweetening is achieved by using amines, by the following reaction:

$$2RNH_2 + CO_2 \rightarrow RNH_3^+ + RNHCOO^-.$$

Reaction occurs in a gas-liquid column at low temperature (40–80°C) followed by amine regeneration at higher temperature (120°C) and low $CO_2$ partial pressure. This reaction requires two moles of amine per mole of $CO_2$ removed. In 1974, Guido Sartori, a chemist at Exxon, realized that by changing the amine, the stoichiometry of the reaction could be changed:

$$RNH_2 + CO_2 + H_2O \rightarrow RNH_3^+ + HCO_3^-.$$

Only one mole of amine is now required per mole of $CO_2$ absorbed. This is potentially a great improvement in efficiency. The stoichiometry can be changed by using a hindered amine, such as diisopropylamine:




The anion formed by reaction with $CO_2$ is destabilized because the side groups have a high electron pushing power and the bulky side chains prevent free rotation of the acid group.

However, if the amine is highly hindered, the rate of reaction becomes so slow that it is useless for $CO_2$ removal. What is required is a moderately hindered amine, such that a reasonable reaction rate is still achieved. This is possible with amines similar to that shown above. However, we do not know exactly which hindered amine to use. Our specifications are likely to go as follows.

1. We require a new product that will double the capacity of the old plant or reduce the size of absorption columns in a new plant. This means that we need to achieve an increase in the $CO_2$ carrying capacity of the absorbing liquid.
2. The rate of reaction must be at least as high as that for the conventional amines, or our capacity gain will be offset by a poor rate of absorption.
3. We want to retrofit the old plant with our new product. Therefore, operating conditions must be similar to those used currently; that is, absorption at 40–80°C, and regeneration at 120°C.
4. In an operating plant, a corrosion inhibitor, containing $V^{5+}$, is present in the absorbing liquid. The hindered amine must be stable in the presence of this inhibitor.

In order to develop the final product, Sartori and co-workers screened a wide range of possible hindered amines for their performance on each of these four criteria.

It is likely that they tested hundreds of possible amines to establish the optimum product. Data on around a dozen hindered amines are published in the open literature, showing the trends established as a function of the size and the chemical nature of the hindering groups.

First, Sartori established that hindered amines can indeed react with the 1:1 stoichiometry shown above. Next, he investigated the rate constants for $CO_2$ absorption. He found that moderately hindered amines showed almost an order of magnitude drop in rate constant relative to unhindered ones and that highly hindered amines were over an order of magnitude worse again. This led to rejection of highly hindered amines in favor of moderately hindered ones. Although the rate constant dropped by changing to hindered amines, the rate of $CO_2$ absorption will be a result of an expression of the form:

$$\text{rate} = k[CO_2]\,[\text{amine}].$$

Because the stoichiometry is 1:1 for hindered $CO_2$ absorption rather than 2:1 for conventional amines, there will be certain operating conditions under which the actual rate of $CO_2$ absorption is higher in the hindered amine case than in the conventional situation. Sartori and his collaborators were able to show that for some moderately hindered amines, this was the case for typical plant operating conditions. Indeed, they found that under these conditions the rate of $CO_2$ absorption was limited only by $CO_2$ diffusion into the liquid. Thus by choosing from a range of moderately hindered amines, the requirement of increased capacity without loss of rate can be met.

Having established the required degree of steric hindering for the amines, the requirements of solubility and thermal stability were satisfied by altering the chemical nature (but not the size) of the side groups. For example, the solubility in aqueous solution is usually enhanced by using alcohol side chains. For this reason, the standard unhindered amine used in conventional $CO_2$ absorption is diethanolamine. Undoubtedly Sartori incorporated similar chemical features into the hindered amine in the final product.

The final stage in the experimental program was to test the stability of the possible amines in the presence of the $V^{5+}$ inhibitor. It turns out that the new product is better than conventional amines in this respect also. The new amines are now produced commercially.

### EXAMPLE 5.2–3 SILVER BULLETS FOR ZEBRA MUSSELS

Zebra mussels are a freshwater mussel native to Europe, which reached North America via bilgewater in cargo ships. They have since become enormously successful, outcompeting native bivalve species and aggressively colonizing freshwater habitats. They present a particular problem to industry because of their propensity to block cooling water systems using raw water supplies, such as power station heat exchangers.

Zebra mussels feed by filtering nutritious particles from the water. It is proposed to control them by feeding them poisoned capsules, "silver bullets," the idea being

to use their own filtering activity as a means of concentrating the poison. This will allow bulk toxic concentrations in the water to be many times lower than that which would be required if the poison were placed directly in the cooling water system. Hence cost and environmental damage should simultaneously be minimized. What further information would be required before this product could be commercially developed?

We must answer two questions:

1. What should the size and composition of our capsules be?
2. What concentration of capsules do we need in order to achieve a given kill rate, say 90%? How does this compare with the bulk water concentration of toxin we would need simply to poison the mussels?

SOLUTION

Question 1 is relatively simple to answer. There is a considerable amount of literature available on toxins for bivalves in general and zebra mussels in particular. One simple but promising candidate is KCl, which induces heart attacks in mussels. Another is the Ethiopian soapberry, which is rich in surfactants and is used extensively for washing clothes in Ethiopia. Waterways used for such washing are remarkably clear of molluscs. We would like to ensure that a mussel is killed if it eats a few silver bullets; we need to establish a lethal dose of each toxin. This will be done by measuring mortality after the direct administration of a given dose to the mussel's gut. We then just need to coat our lethal dose of poison in something edible, probably fat or starch. Because zebra mussels filter only fine particles efficiently, we need to fabricate our capsules in this size range. We would probably finally wish to test our silver bullets in a "live firing" exercise in which the product prototype was administered to feeding mussels and mortality checked.

Question 2 is going to be harder to answer, but crucial to the economic and environmental feasibility of the product. Establishing the fatal concentration of the poisons in solution is a relatively simple experiment. However, establishing the bulk concentration of our poisoned capsules will be harder. We need to know the filtration rate of the mussels in order to be able to calculate their probability of ingesting a silver bullet in a given water flow, such as that inside a heat exchanger. There is some literature on this, but more extensive experiments would certainly be required to mimic the conditions prevalent in industrial pipework.

It is once again clear from this example that taking a product from being a good idea, which we believe will work, to being commercially viable requires a great deal of work and, perhaps more crucially, a lot of time: mussels can take a while to die during experiments! An extensive experimental program to confirm crucial facts or fill in missing or estimated information is indispensable at this stage.

## 6.3 KONČNE SPECIFIKACIJE PRODUKTA

Pred izdelavo produkta (specialna kemikalija, formuliran produkt, naprava...) moramo določiti končne specifikacije produkta. Če načrtujemo kemikalijo, moramo znati natančno opisati njeno molekularno strukturo, njeno končno obliko in zahtevano čistost. Če načrtujemo napravo, moramo znati natančno opisati njeno velikost in obliko ter pričakovan način delovanja.

Priporočljivo je, da končne specifikacije produkta določi jedro projektnega team-a s konsenzom in sicer na osnovi predlogov, ki so jih zapisali člani projektnega team-a.

Pri postavljanju končnih specifikacij:
- še enkrat pregledamo prednosti, ki naj bi jih naš nov produkt imel pred konkurenčnim ali pred našim obstoječim produktom,
- še enkrat ocenimo kako velike so pričakovane izboljšave ter
- še enkrat ocenimo privzete predpostavke in se odločimo, katere predpostavke predstavljajo največjo negotovost za nadaljnji razvoj produkta.

Na takšen način zelo dobro opišemo problem ter identificiramo tehnične omejitve, s katerimi se bomo morali spopasti.

Na tej stopnji se raje poslužujemo načina razmišljanja in reševanja problemov s pomočjo prilagajanja. Našo previdno izbrano ideje želimo izboljšati s pomočjo manjših in premišljenih modifikacij in ne naključnih invencij (inventiven pristop).

Za postavljanje končnih specifikacij se pogosto uporablja strategija s tremi koraki, ki so:

- definicija strukture produkta,

- razvrstitev ključnih lastnosti produkta po pomembnosti,

- pregled kemijskih povodov za velike spremembe v lastnostih produkta.

### Struktura produkta

Specifikacije strukture se za različne produkte močno razlikujejo. V specifikaciji strukture produkta so navadno opisani:

- kemijska sestava. Iz česa je produkt narejen? Če je produkt kemijska spojina, kakšna je kemijska struktura spojine? Če je produkt naprava, koliko se lahko sestava spremeni, da to ne bo vplivalo na delovanje?

- fizikalna geometrija. Katere lastnosti produkta so fiksne? Ali ima produkt fiksne makroskopske dimenzije? Ali je iz tega vidika produkt nenavaden?

- kemijske reakcije. Ali se produkt med uporabo kemijsko spreminja? Ali prisotnost kislin, baz in soli vpliva na lastnosti produkta?

- termodinamika produkta. V kakšni fazi je produkt? Ali je v termodinamsko stabilni ali metastabilni fazi?

**Ključne lastnosti produkta**

Želimo izpostaviti, katere lastnosti produkta so ključne in katera lastnost produkta je najbolj pomembna. Dolg seznam lastnosti se lahko razdeli na tri skupine, ki so:

- strukturne lastnosti. Vključujejo fizikalne lastnosti produkta, kot so trdnost in elastičnost. Te lastnosti so bolj pomembne za naprave kot za kemikalije.

- ravnotežne spremembe. Veliko kemijskih produktov bo spremenilo ravnotežno stanje, ko se bo spremenila temperatura, pH vrednost in druge procesne spremenljivke.

- ključne hitrosti procesov. Hitrost kemijskih reakcij, hitrost prenosa toplote, hitrost toka tekočin, hitrost difuzije...

**Kemijski povodi za spremembe lastnosti produkta**

Identificiramo kemijske spremembe in lastnosti, ki omogočajo, da je produkt aktiven, da deluje. Bolj pomembni so za kemikalije kot za naprave. Ta korak vključuje spremenljivke, ki vplivajo na delovanje produkta, kot so:

- topila in redčila. Topilo topi produkt, da je uporaben. Redčilo redči produkt, da je uporaben (disperzije).

- temperaturne spremembe. Primer je regeneracija produkta (adsorbenta) s segrevanjem ali ohlajanjem.

- kemijske reakcije. Te pogosto potečejo pri spremembi temperature ali pH vrednosti...

- druge fizikalne spremembe, kot je sprememba tlaka, električnega polja...

Ker so si kemijski produkti po naravi zelo različni, se razlikuje tudi pomen posameznih korakov za različne produkte.

Primeri (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**EXAMPLE 5.3–1 FREON-FREE FOAM**

Refrigerators are normally insulated with polyurethane foam. The foam is made by injecting reactive monomers into the space between the inner and outer walls of the refrigerator. Traditionally, freon was injected along with the reagents. As the reaction proceeded, the freon evaporated, producing a foam with about 95% bubbles containing freon.

The result was a very effective insulator. The properties of this insulation were used to establish standards for home refrigerators. The outside dimensions of the refrigerator became standard, so a new refrigerator would easily fit into the space occupied by the old one. The inside dimensions also became standard, so that milk bottles fit conveniently inside. The insulation required for energy efficiency was also legally restricted, with laws based on the properties of freon-containing foam.

However, when freon is released to the environment, it destroys the layer of ozone that protects the earth from excess ultraviolet radiation. As a result, an international agreement has banned the production and use of freon. To be sure, freon in insulating foam seems less abusive than freon in single use products such as hair sprays. Nonetheless, the freon in foam will eventually leak out, perhaps long after the refrigerator has been scrapped. Sensibly, polyurethane foam blown with freon is illegal, and not available.

We need to build refrigerators with the same dimensions and the same degree of insulation as those with freon-containing foam. The degree of insulation achieved depends most dramatically on the thermal conductivity of the gas in the foam's bubbles. This thermal conductivity $k_T$ is given in W/mK by

$$k_T = (0.08/\sigma^2\Omega)\sqrt{T/\tilde{M}},$$

where $\sigma$ is the molecular diameter, in Å; $\Omega$ is dimensionless and of order one, a weak function of temperature; $T$ is the absolute temperature, in °K; and $\tilde{M}$ is the molecular weight in daltons. Thus if we replace the freon with $CO_2$, we find from Table 5.3–1

$$\frac{k_T(CO_2)}{k_T(CCl_2F_2)} = \left(\frac{\sigma_{CCl_2F_2}}{\sigma_{CO_2}}\right)^2\left(\frac{\tilde{M}_{CCl_2F_2}}{\tilde{M}_{CO_2}}\right)^{1/2},$$

$$= \left(\frac{5.3}{3.9}\right)^2\left(\frac{121}{44}\right)^{1/2} = 3.$$

The foam blown with carbon dioxide will provide only one third the insulation of the same thickness of foam blown with freon. A foam blown with nitrogen is even worse, with only one fourth the insulation.

**TABLE 5.3–1 Properties of Gases Used in Insulating Foam**

| Gas[a] | Molecular Weight (d) | Molecular Diameter (Å) | Boiling Point (°C) |
|---|---|---|---|
| Nitrogen ($N_2$) | 28 | 3.8 | −196 |
| Carbon dioxide ($CO_2$) | 44 | 3.9 | −79[b] |
| Freon 12 ($CCl_2F_2$) | 121 | 5.3 | −30 |

[a]Freon's large diameter and high molecular weight give it the lowest thermal conductivity.
[b]Sublimes.

We need a better foam. A careful search for ideas has produced many interesting alternatives, including materials made of many layers of aluminium foil. After careful analysis, however, we decide that our best choice is polyurethane foam modified in some way to reduce its thermal conductivity.

Use the strategy given above to suggest final product specifications.

SOLUTION

The three-step strategy given above suggests defining the product's structure, specifying its chief attributes and identifying any chemical triggers that make the product active. In this case, the chemical trigger is not critical, but the other steps are important.

PRODUCT STRUCTURE. Defining the structure is easy. We want a polyurethane foam containing 95% gas bubbles. The bubbles should be small to avoid free convection: free convection in any larger bubbles will compromise insulation. The idea that the bubbles could be much smaller than in the present foam is interesting, but we defer discussing this until later. There are no chemical interactions in the present foam. Again, the interesting idea of such interactions is deferred until later. In general, foams are metastable, especially if the bubbles are very small, but this should not be a major problem in this case.

THE KEY ATTRIBUTE. The foam is a good internal insulator. This key attribute is directly a result of the thermal conductivity in the foam's gas-filled bubbles. As a result, we can benefit from a review of this transport property. For a monoatomic dilute gas, the thermal conductivity $k_T$ is given by

$$k_T = \frac{1}{3}(\text{distance between collisions})\frac{\text{energy}}{\text{volume}}\left(\frac{\text{volume}}{\text{area time}}\right).$$

The volume per area per time is nothing more than the average molecular velocity, $v$. For a monoatomic gas, this velocity depends on temperature, $T$, via the kinetic energy:

$$1/2\,mv^2 = k_B T,$$

where $m$ is the molecular mass and $k_B$ is Boltzmann's constant. The energy per volume, the product of the molecular concentration $c$ and molar heat capacity $\tilde{C}_v$, is given by

$$c[\tilde{C}_v] = \frac{p}{k_B T}\left[\frac{3}{2}k_B\right],$$

where $p$ is the pressure. We only need to estimate the distance between collisions.

There are two limiting cases of this collision distance, valid for large bubbles and for small bubbles. For larger bubbles, the distance is the mean free path, $\lambda$, that a gas molecule travels before it collides with a second gas molecule. This mean free path is related to the volume per molecule:

$$\begin{aligned}(\pi/4)\sigma^2\lambda &= V/n,\\ &= k_B T/p,\end{aligned}$$

where $\sigma$ is again the molecular diameter, $V$ is the bubble volume, and $n$ is the number of gas molecules in the bubble. Solving for $\lambda$ and combining with the above, we find that

$$k_T = (1/\sigma^2)\sqrt{T/m}.$$

This variation of the thermal conductivity with molecular size and weight is equivalent to that presumed in the problem statement. It is the variation that lets us estimate how much poorer $CO_2$-blown foam would be compared with freon-blown foam.

This large bubble result is dramatically different than that for small bubbles. For small bubbles, the gas velocity and the gas energy per volume are unchanged, but the distance between collisions is different. For small bubbles, this distance is proportional to the bubble diameter. Unlike in large bubbles, where gas molecules collide with each other, a molecule in a small bubble bangs from one point on the wall to another. As a result, the thermal conductivity is now

$$k_T = dp\sqrt{k_B/2mT},$$

where $d$ is the bubble diameter. Note how different this result is from the previous equation. Whereas $k_T$ varies with the inverse square root of molecular weight for both large and small bubbles, $k_T$ increases with temperature in large bubbles but decreases with temperature in small bubbles. More importantly, the thermal conductivity is independent of pressure and bubble size in large bubbles, but it is proportional to the product $(dp)$ in small bubbles. Thus we can make a better freon-free insulating foam by having small bubbles or a low gas pressure.

SETTING FINAL SPECIFICATIONS. To complete our product specifications, we must decide what is a large bubble and what is a small bubble. From the above, we see that this difference depends on the Knudsen number $Kn$, the ratio of the mean free path $\lambda$, and the bubble diameter $d$.

$$\begin{aligned}Kn &= \lambda/d,\\ &= (4/\pi)\sqrt{k_B T}/p\sigma^2 d.\end{aligned}$$

When $Kn \ll 1$, we have intermolecular collisions, and hence large bubbles. When $Kn \gg 1$, we have molecule-wall collisions, and hence small bubbles.

We want small bubbles. Although we can try to make these mechanically, we will find it difficult to get bubbles smaller than 1 $\mu$m, not small enough to be "small." The reason is that the surface energy of such bubbles is high, so that some of the bubbles tend to grow at the expense of others. This process is sometimes called "Ostwald ripening."

However, we could make the bubbles behave as if they were small by reducing the gas pressure, and hence raising the Knudsen number. The product designers who were involved in making a better foam did just this by a very clever invention. They blew rigid polyurethane foam with carbon dioxide in the normal way, under established reaction conditions, but they blew it into a bag made of metal foil. The bag is essentially completely impermeable to all gases. Just before the bag was sealed, the designers added a spoonful of sodium hydroxide to the bag. The sodium hydroxide reacted with any available $CO_2$, which slowly diffused through the foam to react. It turns out that a chemical trigger is involved in our product manufacture after all.

The result was a foam, initially the same as any other $CO_2$-blown foam, but which got better with time. Eventually, as the gas pressure got lower and lower, the foam became a better insulator than the original freon-blown foam which it replaced. The final product specification that the new foam must have a thermal conductivity no higher than freon-blown foam is met.

### EXAMPLE 5.3–2 BETTER BLOOD OXYGENATORS

For open heart surgery, we must use a machine to bypass the patient's heart and lungs while the heart is being repaired. The machine must move the blood at roughly the normal rate, which is relatively easily accomplished with a pump. It must perform the same function as the lungs, a more difficult task: it must add oxygen and remove carbon dioxide. In almost all cases, oxygen addition is more difficult to accomplish than carbon dioxide removal, so that blood oxygenators are normally designed by using oxygen transfer as the benchmark.

We can oxygenate blood by using many familiar chemical engineering operations. For example, we could oxygenate blood in a packed tower, letting blood trickle downward over Raschig rings while air flows upward, countercurrently to the blood. This type of operation is not attractive for two reasons. First, any free interface between air and blood tends to cause clots, just as any open cut on our hands tends to clot. Blood clots can cause strokes. As a result, past designs of blood oxygenators tend to carry out the oxygen transfer across a membrane. Originally, silicone rubber membranes were used that offered significant resistance to mass transfer. More modern designs use microporous hydrophobic membranes that offer no significant resistance to mass transfer.

The second reason that blood oxygenators cannot use conventional equipment such as packed towers is that the volume of blood required to start up such a packed tower would quite literally drain the patient white. The tower could be

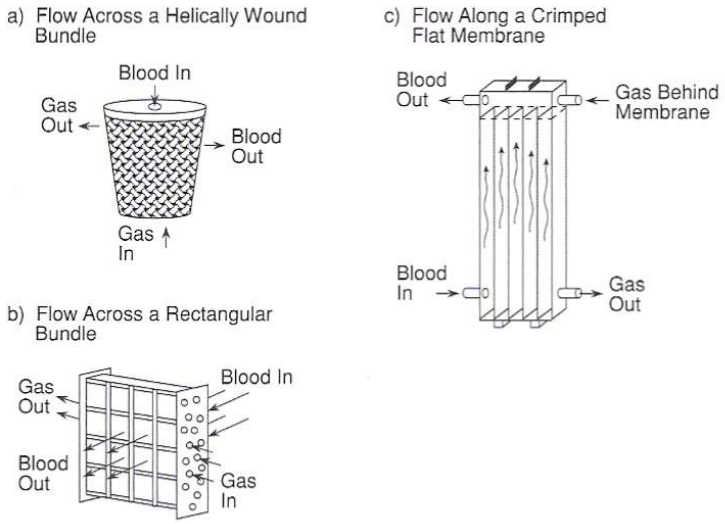



**Figure 5.3–1. Current Commercial Blood Oxygenators.** The designs in a) and b) use beds of air-filled microporous hollow-fiber membranes. The third design, c), uses a crimped, flat, microporous membrane.

started with blood transfusions. Unfortunately, these carry the ever-present risk of infecting the patient with HIV or hepatitis. We must use the smallest blood oxygenators that gives enough oxygen transfer.

Thus, we need a mass transfer device that offers the greatest amount of mass transfer per volume across a microporous membrane. Some designs are shown in Figure 5.3–1. Originally, the membranes used were flat. Later, to get more area, the membranes were corrugated, like furnace filters or the air filters in automobiles. Now, blood oxygenators usually use hollow-fiber membranes, which give the best performance yet achieved.

Imagine that we want to build a new hollow-fiber blood oxygenator that outperforms other models. To do so, we want to maximize the oxygen transferred per blood volume. We know that the oxygen flux per volume $J$ is given by

$$J = Ka(c_1^* - c_1),$$

where $K$ is the overall oxygen mass transfer coefficient, based on a liquid side resistance; $a$ is the membrane area per volume; $c_1^*$ is the blood oxygen concentration at saturation, kept constant by using excess air; and $c_1$ is the actual oxygen concentration in the blood. In this case, $K$ is dominated by the individual mass transfer coefficient in the blood, $k$. Thus, our problem is simple: we must select the oxygenator design that maximizes $ka$.

## SOLUTION

In this example, the key is the product's structure, epitomized by the product $ka$. There are no real chemical triggers; we just need a big $ka$. We begin this selection

**TABLE 5.3–2 Mass Transfer Correlations Across Hollow-Fiber Membranes**

| Flow Geometry | Flow Range | Correlation |
|---|---|---|
| Within fibers | $Sh > 4$ | $Sh = 1.62Gr^{1/3}$ |
| Outside and parallel to fibers | $Gr < 60$ | $Sh = 1.3(\frac{d_e^2 v}{\upsilon l})^{0.9} Sc^{1/3}$ |
| Outside and across fibers | $\mathrm{Re} > 2$ | $Sh = 0.4\,\mathrm{Re}^{0.8} Sc^{0.33}$ |
| Outside and across fiber fabric | $\mathrm{Re} > 2$ | $Sh = 0.8\,\mathrm{Re}^{0.49} Sc^{0.33}$ |

*Note:* Dimensionless groups defined as follows: Graetz number, $Gr = d^2 v/Dl$; Sherwood number, $Sh = kd/D$; Reynolds number, $\mathrm{Re} = dv/\upsilon$; and Schmidt number, $Sc = \upsilon/D$. Variables defined as follows: $d$ is fiber diameter; $v$ is average blood velocity; $D$ is oxygen diffusion coefficient; $l$ is hollow-fiber length; $k$ is mass transfer coefficient in blood; and $\upsilon$ is the kinematic viscosity in blood.

by considering the area per volume $a$. For the hollow fibers, we expect

$$\begin{aligned} a &= \frac{\text{fiber area}}{\text{oxygenator volume}}, \\ &= \left(\frac{\text{fiber area}}{\text{fiber volume}}\right)\left(\frac{\text{fiber volume}}{\text{oxygenator volume}}\right), \\ &= \left[\frac{\pi dl}{(\pi/4)d^2 l}\right](\phi), \\ &= \frac{4\phi}{d}, \end{aligned}$$

where $d$ is the fiber diameter, $l$ is the fiber length, and $\phi$ is the volume fraction of fibers in the module, normally around 0.5. Commercially available microporous hollow fibers typically have a diameter of about 300 $\mu$m. Thus, $a$ is reasonably circumscribed, and any advantages will come from the mass transfer coefficient $k$.

Some of the correlations that are reported for the hollow-fiber mass transfer coefficient are given in Table 5.3–2. In these correlations, the mass transfer coefficient, $k$, is given as a function of many variables, in particular the fluid velocity, $v$. Although this velocity can vary dramatically with the geometry of the hollow fibers, the velocity per length in blood oxygenators is normally fixed:

$$v/l = 1/\mathrm{sec}\,.$$

Higher velocities usually imply higher shear, which can damage the blood.

We can now look at three special geometries of hollow-fiber oxygenators. In every case, we will look at the Sherwood number, for the largest Sherwood number means the largest $k$, and hence the fastest oxygenation. For flow inside the fibers, no matter how the fibers are arranged, we have

$$\begin{aligned} Sh &= 1.62\left(\frac{d^2 v}{Dl}\right)^{1/3}, \\ &= 1.62\left[\frac{(300\times 10^{-4}\,\mathrm{cm})^2\,1\,\mathrm{sec}^{-1}}{10^{-5}\,\mathrm{cm}^2/\mathrm{sec}}\right]^{1/3}, \\ &= 4.5. \end{aligned}$$

In this estimate we have chosen the diffusion coefficient $D$ as $10^{-5}$ cm$^2$/sec, a value typical of water, not blood. Blood's higher viscosity will tend to reduce $D$; and the reactivity of oxygen and hemoglobin will tend to increase the effective value of $D$; but these changes are relatively minor.

As a second alternative, we consider flow outside and parallel to the hollow fibers. In this case, the correlations in the literature vary widely, presumably because it is difficult to manufacture fibers that are evenly spaced. Using the correlation shown, we have

$$\begin{aligned} Sh &= 1.3\left(\frac{d^2v}{\upsilon l}\right)^{0.9}\left(\frac{\upsilon}{D}\right)^{1/3} \\ &= 1.3\left[\frac{(300\times10^{-4}\text{ cm})^2\,1\text{ sec}^{-1}}{10^{-2}\text{ cm}^2/\text{sec}}\right]^{0.9}\left(\frac{10^{-2}\text{ cm}^2/\text{sec}}{10^{-5}\text{ cm}^2/\text{sec}}\right)^{1/3} \\ &= 1.5, \end{aligned}$$

where we have assumed the kinematic viscosity, $\upsilon$, is close to the value of water of 0.01 cm$^2$/sec. The value we calculate is significantly less than that for flow within the hollow fibers, so this geometry is not attractive.

Our third alternative looks at flow outside but perpendicular to the hollow fibers. From our experience with flow outside but parallel to the fibers, we expect that the fibers should be as evenly spaced as possible. One good way to do so is to weave the fibers into a hollow-fiber fabric. In this case,

$$\begin{aligned} Sh &= 0.8\left(\frac{dv}{\upsilon}\right)^{0.49}\left(\frac{\upsilon}{D}\right)^{0.33}, \\ &= 0.8\left(\frac{300\times10^{-4}\text{ cm }4\text{ cm/sec}^{-1}}{10^{-2}\text{ cm}^2/\text{sec}}\right)^{0.49}\left(\frac{10^{-2}\text{ cm}^2/\text{sec}}{10^{-5}\text{ cm}^2/\text{sec}}\right)^{0.33}, \\ &= 30, \end{aligned}$$

where we have assumed that the hollow fibers are arranged in a bed whose depth is 4 cm, so the blood velocity is 4 cm/sec. This looks like the best geometry by far.

When we look at the selection of commercial blood oxygenators shown in Figure 5.3–1, we see that most current successful designs do use blood flow across beds of air-filled hollow fibers. We are not likely to improve on these geometrics, especially because the blood flows are carefully controlled to avoid excessive shear. To be commercially innovative, we will need to select a design that has additional advantages beyond maximizing oxygen transfer per oxygenator volume. Because such a new product may be hard to design, we should consider canceling this project.

Znanja potrebna za izdelavo kemijskih produktov, kot so formulirani produkti in naprave s kemijsko ali fizikalno spremembo, so temeljna znanja kemijskega inženirstva in kemije. Na tem mestu bomo izpostavili samo nekatere primere.

## 6.4 MIKROSTRUKTURIRANI (FORMULIRANI) PRODUKTI

Tipična predstavnika formuliranih produktov sta sladoled in premaz. Ključni lastnosti teh produktov sta »kremoznost« in »prekrivna moč«, ki sta odvisni od mikrostrukture produkta. Kremoznost sladoleda je odvisna od velikosti ledenih kristalov, ki so veliki okoli 8 μm. Prekrivna moč premaza pa je odvisna predvsem od povprečne velikosti (okoli 2 μm) in porazdelitve delcev lateksa. Čeprav je pomembna tudi kemijska struktura produkta na molekularnem nivoju, je v takšnih primerih za uporabne lastnosti ključna struktura na mikronivoju.

Mikrostrukturirani produkti so kemijsko kompleksni. Tipični sestavi mleka in premaza na vodni osnovi sta prikazani v tabelah 5.4-1 in 5.4-2.

Tabeli 5.4-1 in 5.4-2 (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**TABLE 5.4–1 Average Properties of Milk**

| Component | Concentration (wt. %) |
|---|---|
| Water | 82.0 |
| Fat, including saturated and unsaturated fatty acids | 4.0 |
| Protein, which emulsifies the fat | 3.4 |
| Lactose | 4.8 |
| Other solids | 0.8 |

*Note:* Milk is an oil-in-water emulsion, with about $3 \times 10^9$ globules/cm$^3$ of around 4 $\mu$m diameter. The overall composition is shown.

**TABLE 5.4–2 Typical Formulations for Latex Paints**

| Component | Exterior (wt. %) | Interior (wt. %) |
|---|---|---|
| Pigment ($TiO_2$), to scatter light | 20 | 11 |
| Extenders, including clays | 16 | 34 |
| Polymers, for rheology control | 18 | 16 |
| Latex, to form coating | 25 | 10 |
| Defoamers, Dispersants, Buffers, etc. | 4 | 3 |
| Water | 17 | 26 |

*Note:* Latex particles average 0.5 $\mu$m; smaller sizes give higher gloss, but larger sizes give greater opacity and better flow.
From Stokes and Evans, 1996.

Mikrostrukturirani produkti so navadno v metastabilnem stanju. To pomeni, da njihove lastnosti (uporabne in strukturne) niso odvisne samo od pogojev trenutnega stanja (spremenljivk stanja: temperatura, tlak...), ampak tudi od načina izdelave oziroma procesnih parametrov, pri katerih so bili izdelani (od poti po kateri je bilo stanje doseženo) (Procesna funkcija). Kljub velikemu pomenu procesne poti, lahko številne lastnosti mikrostrukturiranih produktov razložimo s klasičnimi kemijsko-inženirskimi orodji, kot so termodinamika, kinetika in mešanje (Tabela 5.4-3).

Tabela 5.4-3 (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**TABLE 5.4–3 Key Ideas for Microstructured Products**

| Intellectual Basis | Key Concepts | Products Where Important |
|---|---|---|
| Thermodynamics | Electrochemical potential | Water softeners |
| | Micelle formation | Soap and detergents |
| | Ostwald ripening | Ice cream |
| Kinetics | Colloid stability | Paint, bearnaise sauce |
| | Colloid inversion | Suntan lotion, butter |
| Rheology and Mixing | Dimensionless groups | Ice cream, floor wax |

*Note:* Many of these ideas, which are parts of colloid chemistry, are infrequently stressed in introductory chemistry and chemical engineering courses.

**Termodinamika**

Termodinamiko mikrostrukturiranih produktov najlažje razložimo s pomočjo kemijskega potenciala. Kvalitativno je kemijski potencial energija posamezne specije. Ta energija je Gibbsova prosta entalpija (energija) za mol, ki vključuje entalpijski in entropijski prispevek. Kemijski potencial navadno narašča s temperaturo in tlakom (tlak ima majhen vpliv, če je specija v kapljevinasti fazi). Kemijski potencial se navadno znatno zniža, ko specijo raztopimo v topilu. Topnost pa je omejena, če topljenec in topilo nista kompatibilna – nimata enakih topnostnih parametrov.

Kvantitativen zapis kemijskega potenciala za raztopine:

$$\mu_1 = \mu_1^0 + RTlnx_1 + \omega x_2^2$$

kjer je $\mu_1$ kemijski potencial v J/mol, $\mu_1^0$ kemijski potencial v standardnem stanju, $R$ splošna plinska konstanta, $T$ temperatura, $\omega$ merilo za toploto mešanja, ter $x_1$ in $x_2$ molska deleža topljenca in topila. V tem primeru je standardno stanje čista komponenta 1 pri dani temperaturi T in tlaku P.
Logaritemski člen v enačbi je negativen, ker je $x_1$ manjši od 1, in predstavlja zmanjšanje kemijskega potenciala na račun redčenja – idealnega raztapljanja. Za endotermno raztapljanje je $\omega$ pozitiven. Pomeni, da je za raztapljanje potrebna toplota, kar pomeni višji kemijski potencial.

Podobna enačba velja za raztopine polimerov z visoko molekulsko maso. V spodnji enačbi je specija 1 topilo in specija 2 polimer:

$$\mu_1 = \mu_1^0 + RTln\phi_1 + RT\phi_2 + \chi\phi_2^2$$

kjer sta $\phi_1$ in $\phi_2$ volumska deleža topila in polimera in $\chi$ je merilo za toploto mešanja. Člen $RT\phi_2$ je korekcijski člen za polimerne raztopine (ker so molekulske mase polimera velike in se zato slabše mešajo s topilom kot majhne molekule), ki zvišuje kemijski potencial.

Kemijski potencial lahko opiše tudi obnašanje koloidnih raztopin, kot sta nastanek micel v vodi in »Ostwald ripening« efekt. Micele tvorijo molekule emulgatorja (kot je natrijev dodecilsulfat, $CH_3(CH_2)_{11}SO_3^-Na^+$), ki imajo polarno glavo in dolg nepolaren rep, v vodni raztopini emulgatorja pri koncentracijah nad kritično micelno koncentracijo. Micele so skupki, v katerih notranjost so usmerjeni nepolarni repi molekul emulgatorja, medtem ko je površina micel, ki je v stiku z vodo, sestavljena iz polarnih glav molekul emulgatorja. Prisotnost micel zniža kemijski potencial emulgatorja. Še več, v notranjosti micel se nahajajo (so topne) nepolarne molekule, ki niso topne v vodi. (»Topnost« holesterola v vodi se poveča za 30 000 000 krat, če so v vodi micele.)

Model »separacije faz« predpostavlja, da so micele ločena faza. Ko je dosežena kritična micelna koncentracija emulgatorja ($x_{1c}$), se začnejo tvoriti micele. Takrat je kemijski potencial:

$$\mu_{1(micele)} = \mu_1^0 + RTlnx_{1c}$$

Nad kritično micelno koncentracijo se emulgator ne bo več raztapljal v vodi, ampak bo tvoril micele.

Micele so termodinamsko stabilna faza. Ko micele rastejo, na račun akumulacije nepolarnih snovi v njihovi notranjosti, nastanejo termodinamsko stabilne mikroemulzije, ki so največkrat metastabilne. Primeri takšnih emulzij so mleko, tekoče čistila, premazi na vodni osnovi..., ki ostajajo dolgo metastabilni (leta).

Tudi »Ostwald ripening« efekt kristalov vode v sladoledu se lahko opiše s pomočjo enačbe za kemijski potencial vode v kristalih:

$$\mu_{1(voda\ v\ kristalih\ premera\ r)} = \mu^0_{1(voda\ v\ večjih\ kristalih)} + \frac{2\sigma}{r}$$

kjer je $\sigma$ površinska napetost. Enačba pove, da so termodinamsko bolj stabilni veliki kristali, ker je takrat vrednost kemijskega potencila nižja. To je za sladoled slabo, ker mali kristali težijo k združevanju v večje (»Ostwald ripening« efekt). Tega procesa ne moremo preprečiti, lahko pa ga upočasnimo. V sladoledu, lahko k zakasnitvi pripomorejo kristali maščob, ki so prav tako prisotni.

**Kinetika**

Stabilnost koloidov

Glavno vprašanje, ko obravnavamo stabilnost koloidov, je, koliko časa so lahko produkti v metastabilnem stanju. Kdaj se bo mikrostruktura produkta, ki zagotavlja želene lastnosti, porušila?

Primer faznega diagrama je prikazan na sliki 5.4-1a. Diagram prikazuje odvisnost temperature od sestave binarne zmesi (topilo-topljenec). Pri visoki temperaturi imamo eno fazo. Pri nižjih temperaturah, pod ravnotežno črto ali binodalno krivuljo imamo navadno dve fazi, nasičeno raztopino topljenca v topilu in čisto trdno snov (topljenec). Pri nizkih temperaturah imamo fizikalno mešanico zmrznjenega topila in topljenca.

V praksi se lahko zgodi, da pri ohlajanju čez binodalno krivuljo, topljenec ne izpade iz topila. Raztopina postane in ostane prenasičena dalj časa. Vzrok za to je mogoče razbrati iz slike 5.4-1b. Ko se raztopina ohlaja pod binodalno krivuljo, bi imela manjšo energijo, če bi topljenec precepitiral iz raztopine. Vendar, da se to lahko zgodi, se morajo najprej tvoriti majhni kristali. Majhni kristali pa imajo višjo energijo. Zato bo do separacije faz prišlo samo, če bo v prenasičeni raztopini prisotnih

nekaj večjih kristalizacijskih jeder, mogoče prahu ali kristalov drugega topljenca, kar bo premagalo energijsko bariero ter omogočilo nastajanje večjih delcev.

Seveda tudi stanje prenasičenosti ne traja večno. Ko temperatura še naprej pada, se niža tudi krivulja proste energije topljenca v odvisnosti od velikosti kristalov (manjšajo se velikosti kristalov pri isti prosti energiji topljenca). Če se krivulja zniža toliko, da postane velikost kristalov, ki je zahtevana za fazno separacijo, manjša od velikosti kristalov, ki nastanejo pri naključnih molekularnih fluktuacijah, postane sistem nestabilen. Omenjeni pogoji so spinodalni pogoji, pri katerih precepitira iz prenasičene raztopine. Dobimo dve fazi.

Področje med krivuljo, ko je fazna separacija mogoča (binodalno kriuljo), in krivuljo, ko je fazna separacija neizogibna (spinodalno krivuljo), je metastabilno področje.

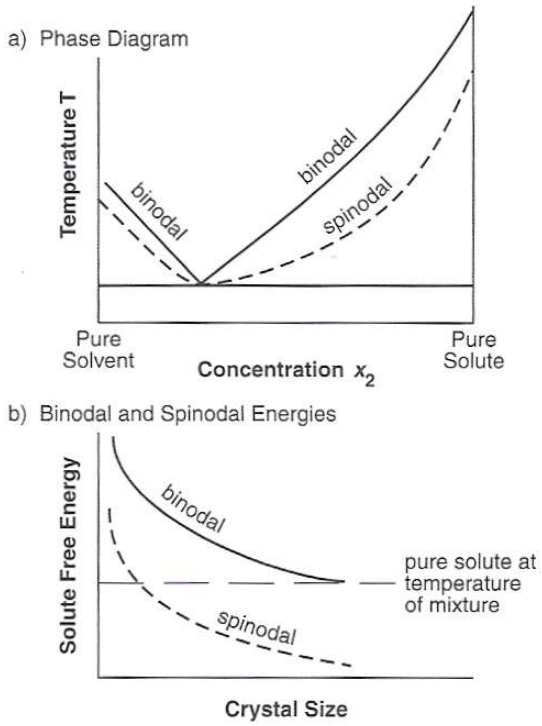



**Figure 5.4–1. Binodal and Spinodal Lines in Crystallization.** The equilibrium phase diagram, shown in a), has a metastable region between the binodal and spinodal. This region is the result of the increased surface energy of smaller crystals, as suggested in b).

Podobna metasabilna področja so značilna za koloide, kot sta mleko in premaz na vodni osnovi (slika 5.4-2). Na sliki je prikazana potencialna energija koloidnih delcev v odvisnosti od razdalje med njimi.

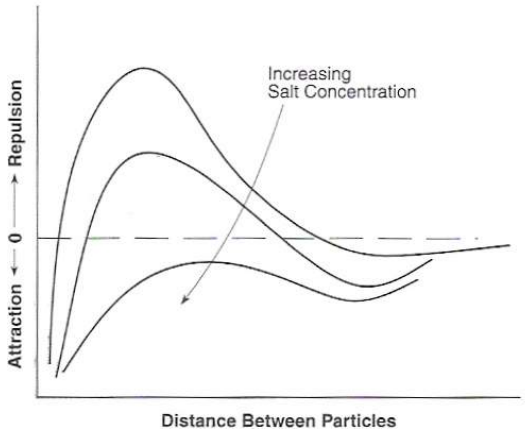



**Figure 5.4–2. Stability of Colloidal Suspensions.** As they get closer, colloidal particles are first attracted, then repelled, and finally irreversibly attracted. The repulsion can be reduced by adding salt.

Ko so delci daleč narazen, ni interakcij med njimi. Ko so si delci bliže, se delci z nasprotnim nabojem privlačijo. Ko se delci bolj približajo, se začno odbijati. Če se pod vplivom neke zunanje sile, delci še zbližajo, se spet privlačijo, še bolj zbližajo in aglomerirajo. Težnjo k aglomeraciji povečamo z dodatkom soli v koloidno raztopino.

V metastabilnem stanju velja:

$$\frac{[koncentracija\ soli][naboj\ protiiona]^6}{[temperatura]^5} \leq konstanta.$$

Delci aglomerirajo, če je leva stran enačbe večja od konstante.

Ko je sistem destabiliziran, je hitrost aglomeracije velika. Enačba za hitrost zmanjševanja števila delcev je drugega reda:

$$\frac{dN}{dt} = -kN^2$$

kjer je *N* število delcev na volumen in k hitrostna konstanta (l/(s · št. delcev) , ki je

$$k = 8\pi Dd,$$

kjer je *D* difuzivnost koloidnega delca in d premer delcev. Ker pa v odsotnosti elektrostatskih efektov (ko dodamo sol) velja Stokes-Einsteinova enačba:

$$D = \frac{k_B T}{3\pi\eta d}$$

kjer je $\eta$ viskoznost topila. Zato je *k*:

$$k = \frac{8k_B T}{3\eta}$$

**Reologija tekočin in mešanje**

Pri izdelavi in uporabi mikrostrukturiranih produktov, kot so koloidi, je pomembno poznavanje njihovega toka in reologije. Reologija mikrostrukturiranih produktov se razlikuje od reologije Newtonskih tekočin.

Na sliki 5.4-3 je prikazana odvisnost hitrosti toka Newtonske in ne-Newtonske tekočine (katere viskoznost s hitrostjo toka pada) od uporabljene sile. Slika 5.4-4 prikazuje odvisnost strižne napetosti od strižne hitrosti. Za Newtonsko tekočino je pri visokih hitrostih značilen turbulenten tok. Za mikrostrukturirane produkte turbulenten tok ni značilen (je redkost).

Naklon krivulj na sliki 5.4-4 je viskoznost ($\eta$).

$$\tau = -\eta \cdot \frac{dv}{dz}$$

Viskoznost Newtonskih tekočin je konstanta in neodvisna od strižne hitrosti v laminarnem območju.
Viskoznost ne-Newtonskih tekočin ni konstanta in je odvisna od strižne hitrosti v laminarnem območju. Mikrostrukturirani produkti, katerim viskoznost z naraščanjem strižne hitrosti pada (»shear thinning« obnašanje), imajo zato nekatere prednosti iz uporabnega vidika. Na primer ko premaz

nanašamo s čopičem na steno, je strižna hitrost zaradi premikanja čopiča visoka in navidezna viskoznost premaza nizka. Pomeni, da lahko premaz enakomerno nanesemo na steno. Po nanosu premaza želimo, da ta ostane na steni (da ne zdrsi pod vplivom gravitacije s stene). To omogoča navidezno visoka viskoznost premaza pri nizkih strižnih hitrostih zaradi gravitacije.

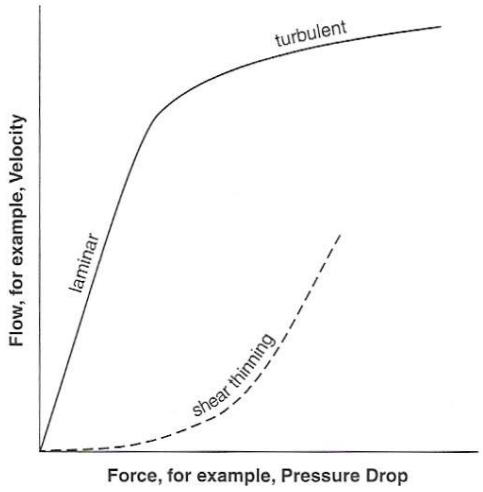



**Figure 5.4–3. The Relationship Between Force and Flow.** The solid curve represents Newtonian flow. The dashed curved describes flow of a shear thinning, non-Newtonian fluid.

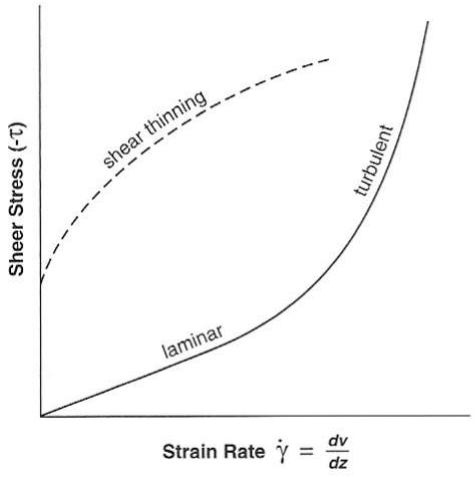



**Figure 5.4–4. The Relationship Between Shear Stress and Shear Rate.** The force in the previous figure is more exactly represented as a stress, i.e., a force per area. The velocity is better described as its gradient, on strain rate. As in the previous figure, the solid and dashed curves are for Newtonian and non-Newtonian fluids, respectively.

Vzrok za ne-Newtonsko obnašanje mikrostrukturiranih kapljevin je prav njihova mikrostruktura.
V premazu na vodni osnovi, ki je koloidna raztopina, se pri višjih strižnih hitrostih porušijo vodikove vezi med surfaktantom (ki je na površini delcev) in vodo. Zato se zniža viskoznost.
Viskoznost marsikaterega čistilnega sredstva je pri višjih strižnih hitrostih nižja, ker se takrat poruši struktura tekočih kristalov.

Po drugi strani pa ne-Newtonsko obnašanje mikrostrukturiranih produktov otežuje mešanje takšnih tekočin (Še zlasti pri proizvodnji ali uporabi v industrijskem merilu.). Takrat je obravnava mešanja kompleksna in naš glavni problem so povečevalni kriteriji: Kako v industrijskem merilu doseči enako mešanje kor v laboratorijskem merilu?

Mešanje visoko viskoznih tekočin navadno poteka v laminarnem tokovnem režimu. V tem primeru nimamo splošnega pravila za povečevanje mešanja. Povečujemo glede na rezultat mešanja.

Mešanje nizko viskoznih tekočin navadno poteka v turbulentnem tokovnem režimu, kjer je čas mešanja ($t_M$) podan:

$$t_M = \frac{l^2}{4D}$$

kjer je D difuzivnost specije, ki jo mešamo, in l velikost vrtinca. Ker je D neodvisna od velikosti mešalnika, bomo pri povečevanju obdržali enako velikost vrtinca, ki pa je

$$l \propto \left(\frac{\rho v^3}{P/V}\right)^{0,25}$$

kjer je $\rho$ gostota produkta, $\nu$ kinematična viskoznost produkta ter P/V vnos moči na volumen v mešalniku. Ker sta snovni lastnosti konstantni, bo povečevalni kriterij volumski vnos moči. P/V mora biti enak za laboratorijski in industrijski mešalnik.

Primeri (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**EXAMPLE 5.4–1 DESTABILIZING LATEX PAINT**

A particular latex paint contains 20% by volume of 0.6-$\mu$m polymer particles. Smaller particles give a paint with more gloss; larger particles give a paint with more hiding power. When this paint is spread, the water in the emulsion evaporates, the colloid becomes unstable, and the particles fuse into a single smooth layer. In cases in which the paint is used at temperatures below the glass transition of the polymer, the polymer particles must be plasticized so that they fuse easily. This fusion is why a latex paint is hard to clean off after it dries, even though the original colloid is easily wiped up.

Paints like this are normally stabilized by surfactants, especially polyphosphates. In some cases, however, the surfactants can phase separate, and the colloid becomes unstable. Freezing can cause such an instability. If it becomes unstable, how long will it take for the paint to agglomerate?

SOLUTION

The easiest way to see how long the paint takes to agglomerate is to use Equation 5.4–8 to calculate the time to cut the particle concentration in half. To make this calculation, we need to find the original concentration, $N_0$, and the rate constant, $k$. This concentration is

$$N_0 = \frac{\text{number of particles}}{\text{volume of paint}} = \left(\frac{\text{volume of particles}}{\text{volume of paint}}\right)\left(\frac{\text{number of particles}}{\text{volume of particles}}\right),$$

$$= \phi\frac{1}{[4/3\pi(d/2)^3]} = 0.2\frac{1}{\{4/3\pi[(0.6\times10^{-4}\,\text{cm})/2]^3\}} = 1.8\times10^{12}\,\text{cm}^{-3}.$$

From Equation 5.4–11, we can find the rate constant:

$$k = \frac{8k_BT}{3\mu} = \frac{8[1.38\times10^{-16}(\text{g cm}^2/\text{sec}^2\,{}^\circ\text{K})]273{}^\circ\text{K}}{3(0.01\,\text{g/cm sec})} = 10\times10^{-12}\,\text{cm}^3/\text{sec}.$$

Thus

$$t_{1/2} = \frac{1}{kN_0} = 0.05\ \text{sec}.$$

The number of particles is cut in half in 1/20 sec. Once the metastable colloid goes unstable, its collapse is catastrophic.

## EXAMPLE 5.4–2 MAKING MORE ICE CREAM

A process for making ice cream, shown in Figure 5.4–5, begins by mixing the ingredients. After pasteurization, these ingredients are homogenized under high shear, and then cooled. The mixture is aged to allow fat crystals to form. It is

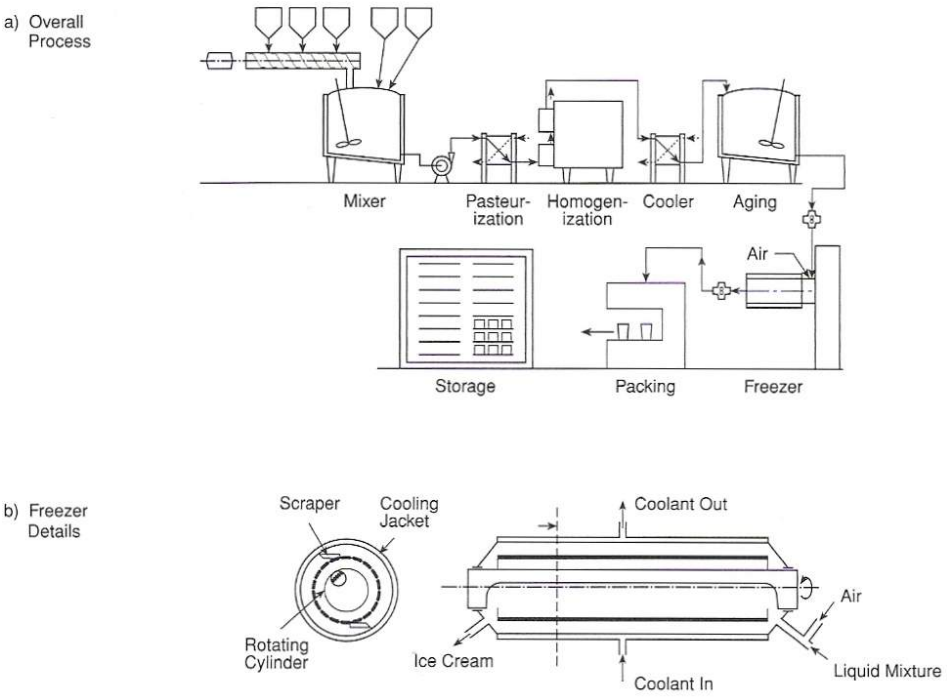



**Figure 5.4–5. Schematic Diagram of a Process for Ice Cream Manufacture.** As shown in a), the process begins with mixing, pasteurization, and cooling. Then, the ice cream is aged to allow metastable fat crystals to form. These stabilize the air added during freezing, and hence improve shelf life. Freezer details are given in b).

then aerated and pumped into the channel of an annularly shaped freezer. The outside of the freezer is chilled; the inside annular core rotates, scaping the outer surface with a helically shaped paddle. The extruded ice cream is then packaged and stored at low temperature to retard Ostwald ripening of the ice crystals.

You have been successfully operating a small ice cream plant, and are now thinking of building a new plant that is three times as large. How should you scale up the various mixing operations?

### SOLUTION

To increase mixer volumes, and yet keep the same geometry, the diameter and heights of all tanks should increase $3^{1/3}$, or a factor of 1.44. The liquid mixture will have low viscosity, so in order to duplicate the original mixing, the homogenization and the aeration should use the same power per volume in the large tank as in the small one. You also want to use the same residence time in the new larger aerator as in the old one.

The difficulty may be the freezer. There, we want three times the surface area at the same shear rate as before. If we keep the residence time the same, the length must be unchanged, so the diameter of the freezer must triple. The power required in the larger freezer will also triple. The equipment cost for making ice cream will be reduced in the larger equipment, but not by as much as for most commodity chemical processes.

## 6.5 IZDELAVA NAPRAV

Naprave, ki proizvajajo kemijsko reakcijo, največkrat delujejo analogno (na osnovi istih principov), kot naprave, ki jih uporabljamo kot procesno opremo v kemijskem inženirstvu. Zato so znanja, ki jih potrebujemo za njihovo načrtovanje, klasična znanja procesnega kemijskega inženirstva (osnovne operacije).

Temeljni inženirski principi za načrtovanje naprav so prikazani v tabeli 5.5-1.

**TABLE 5.5–1 Typical Engineering Principles for Device Design**

| Intellectual Basis | Key Concept | Product |
|---|---|---|
| Thermodynamics | *Osmotic pressure* | Osmotic pump for drug delivery |
| | *Electrochemical potential* | pH electrode |
| | Heat of reaction | Wraps for sports injuries |
| Transport phenomena | Fluid flow | Infusion of physiological saline |
| | Film diffusion | Controlled drug release, slow release fertilizer |
| Unit operations | Heat transfer | Sleeping bags |
| | Mass transfer | Coffee maker, artificial kidney |
| | Heat and mass transfer | Home humidifier, heart-lung machine |
| Reaction engineering | *Enzyme reaction* | Glucose sensor, pregnancy test |
| | Nucleation | Smoke alarm |

*Note:* The concepts that are italicized are those reviewed in this section.

Pri načrtovanju naprav smo osredotočeni predvsem na to, kako in iz katerih delov bo naprava zgrajena. Pomagamo si z izrisanim načrtom naprave in njenih delov.

Primera (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

## EXAMPLE 5.5–1 AN ELECTRODE FOR MEASURING DODECYL SULFATE

An electrode for this anion consists of three basic parts: an inner filling solution, a liquid membrane, and the solution being tested. The inner solution is just 0.01 M of NaCl around an Ag/AgCl electrode. The liquid membrane consists of a chlorinated aromatic solution containing tributylhexadecylammonium chloride stabilized in a microporous support. The measurement also uses a second reference electrode that need not concern us here.

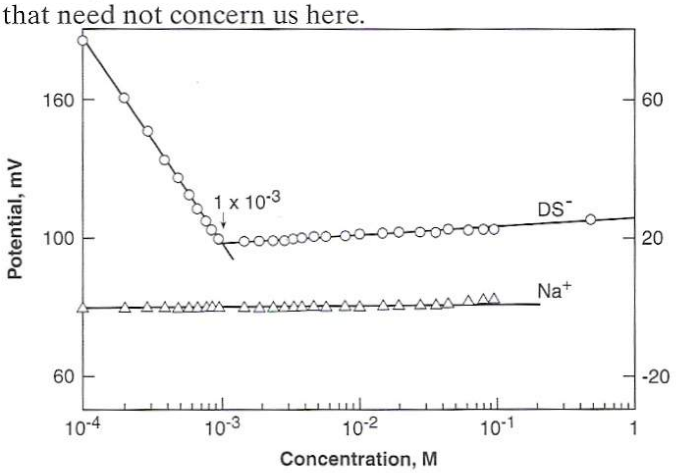



**Figure 5.5–1. Electrochemical Potentials Measured for Sodium Dodecyl Sulfate with Added Sodium Chloride.** The circles are the measured dodecyl sulfate's potentials. The triangles are the measured sodium potentials minus those found in the appropriate solutions containing only sodium chloride.

Data taken with this electrode are shown in Figure 5.5–1. Explain what these data mean.

### SOLUTION

At low concentrations, the data are exactly what we should expect, showing a slope close to the Nernst limit of 59 mV per decade change in concentration. At a concentration close to $10^{-3}$ M, however, the data change abruptly, and the potential difference seems to become almost independent of concentration.

These data are consistent with micelle formation. At low concentrations, the dodecyl sulfate ions are unassociated and behave like other normal anions. Above a "critical micelle concentration" (cmc), in this case about $10^{-3}$ M, these anions associate into micelles, as discussed in the previous section. As more dodecyl sulfate anion is added, it does not go into solution, but into this aggregated phase. Thus the dilute data show that this detergent electrode is working, and the concentrated data give a detailed picture of micelle formation.

## EXAMPLE 5.5–2 DESIGNING AN OSMOTIC PUMP

Drugs are often given orally, as pills taken every few hours. In many cases, this means that drug concentrations in the blood can fluctuate widely. Just after the pill is taken, the drug concentration jumps, sometimes briefly beyond the toxic limit. (In France, this is called "le burst effect.") After an hour or two, the drug concentration wanes, often dropping below the concentration where it is effective. Thus for many drugs, the blood concentration is occasionally too high and often too low, only periodically passing through the desired range.

These concentration variations have sparked many inventions aimed to provide a steady drug release. One such invention, shown in Figure 5.5–2, is called

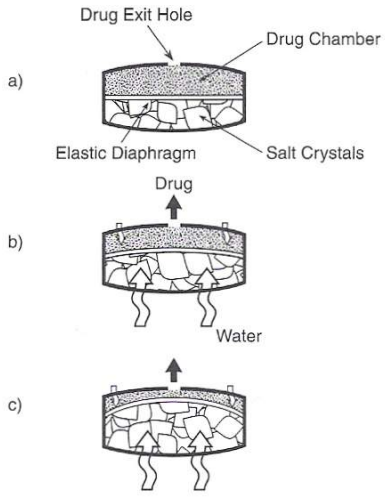



**Figure 5.5–2. An Osmotic Pump.** This device has a rigid casing separated into two compartments by an elastic diaphragm. Water, pulled into the pump by osmosis, distends the diaphragm and steadily ejects the drug.

an "osmotic pump." The pump consists of a rigid housing capped with a semipermeable membrane. The housing is partially filled with a balloon, which in turn is filled with a solution of the drug whose delivery is to be controlled. The rest of the housing is filled with saturated brine in which sodium chloride crystals are suspended.

When this device is surgically implanted in the human body, the difference in osmotic pressure between the blood and the brine causes a water flow across the semipermeable membrane. The amount of the flow is proportional to the concentration difference across the membrane. The concentration difference of brine across the membrane stays constant because the brine inside the pump contains suspended salt crystals and these crystals dissolve as water flows in. Because the concentration difference stays constant, the flow is constant; because the flow is constant, the balloon is squeezed constantly to release drug solution. The beauty of this device is that the constant release of drug solution does not depend on the drug's properties, but only on those of brine and the membrane.

To design such a device, we plan to use a semipermeable membrane that has a reported permeability (defined as volume flux per unit pressure difference across the membrane) of $10^{-10}$ cm/sec kPa. What membrane area do we need to supply a release of 0.8 $\mu$L/hr?

SOLUTION

Saturated sodium chloride at a body temperature of 37°C has a concentration of about 5.4 mol/dm$^3$. Thus the osmotic pressure is

$$\Delta\Pi = c_1 RT = 2 \times \left(\frac{5.4\,\text{mol}}{10^{-3}\,\text{m}^3}\right) \times \frac{8.31\,\text{J}}{\text{mol}\,^\circ\text{K}} \times 310^\circ\text{K} = 28{,}000\,\text{kPa}.$$

The factor of two is the result of ionization. This pressure is high, almost 300 atm. The flux is

$$N_1 = \frac{1 \times 10^{-10}\,\text{cm}}{\text{sec kPa}}(28{,}000\,\text{kPa}) = 2.8 \times 10^{-6}\,\text{cm}^3/\text{cm}^2\ \text{sec}.$$

Thus the membrane area, $A$, is given by

$$\frac{0.8 \times 10^{-3}\,\text{cm}^3}{3600\,\text{sec}} = \frac{2.8 \times 10^{-6}\,\text{cm}^3}{\text{cm}^2\,\text{sec}} \times A;$$

$$A = 0.08\,\text{cm}^2.$$

This corresponds to a circular patch about 3 mm across.

## 6. 6 IZDELAVA SPECIALNIH (POSEBNIH) KEMIKALIJ

Ključne uporabne lastnosti specialnih kemikalij izvirajo iz njihove kemijske strukture na molekularnem nivoju. Za izdelavo kemikalij moramo poznati njihovo kemijsko sintezo iz reaktantov. Sintezo navadno razvijejo kemiki.

Kemijski inženir zbere rezultate, ki mu jih posredujejo kemiki, in jih preveri. Nato razvije reakcijsko inženirstvo za proizvodnjo (izdelavo) kemikalij. Izračunati mora, koliko produkta se lahko proizvede v določenem času (kemijska kinetika). Izbrati mora najbolj primerno vrsto procesa za sintezo (kako dodajati reagente, kakšen bo reaktor, kakšni bodo procesni pogoji...). Izbrati mora separacijske tehnike in naprave za čiščenje produkta. Laboratorijsko sintezo in separacijo mora prenesti na industrijski nivo.

### 6.6.1 Razširitev laboratorijskih rezultatov in reakcijsko inženirstvo

Za specialne kemikalije je značilno, da jih proizvedemo v manjših količinah in da imajo višjo ceno kot proizvodne kemikalije. Življenjska doba kemijskih produktov, kar so specialne kemikalije, je relativno kratka in zelo pomembno je, da je produkt v čim krajšem času na tržišču (da smo prvi). Zaradi omenjenega specialne kemikalije sintetiziramo v generičnih reaktorjih in čistimo v generičnih separatorjih. Navadno so reaktorji šaržni in primerni za sintezo več različnih kemikalij. Optimizacija sinteze in separacije ni ključnega pomena. Ključno je, da smo hitri in da lahko naredimo več različnih produktov.

#### Razširitev laboratorijskih rezultatov

Rezultat kemika je uspešna laboratorijska sinteza manjše količine specialne kemikalije z dokazano aktivnostjo. Naloga kemijskega inženirja je, da sintezo izboljša tako, da bomo dobili več produkta. Potrebna je komunikacija s kemikom, ki je pogosto podobna spodnji:

**Chemist:** This is an easy reaction which anyone intelligent should be able to run. I just dissolve the crude steroid in methylene chloride and then add *n*-butyl lithium. The reaction is . . . Wait, let me put it in terms you'll understand. At −40°C,

$$A + B \rightarrow AB.$$

You can't run too long because there's a side reaction:

$$AB + B \rightarrow AB_2.$$

I then add acetone, which knocks out the product (i.e., causes it to precipitate). I decant the solvents and add DMF (dimethylformamide) to redissolve it. Then I add water to make the alcohol:

$$AB + H_2O \rightarrow AOH + BH.$$

All these reactions are pretty exothermic. Still, they run easily, though the overall selectivity is often low, around 40%. You shouldn't have any trouble getting that higher.

**Engineer:** Why is the selectivity so low?

**Chemist:** I don't know. It often is in reactions like these.

**Engineer:** How much does the temperature increase?

**Chemist:** Quite a lot. Even at −40°C, you can see the temperature jump when you add the *n*-butyl lithium. However, I've kept the temperature rise small by running in an acetone-$CO_2$ bath. Sometimes, I've kept it from jumping too much by turning off the stirrer for a while.

**Engineer:** Can you use any different solvents?

**Chemist:** I don't know. You probably can't replace methylene chloride; it really is the best for these reactions.

**Engineer:** You remember that it's viewed as a dangerous carcinogen.

**Chemist:** Yeah, but lots of chemicals are dangerous.

**Engineer:** Could methylene chloride be replaced with butyl acetate?

**Chemist:** I don't know. Look: I really like methylene chloride. It works really well and I think you'll have trouble replacing it.

**Engineer:** Did you ever check for the maximum temperature rise in this reaction?

**Chemist:** No, but it could be big, enough to boil the solvent. But you can slow the reaction by shutting down the stirring.

**Engineer:** Does that work if the reaction mixture starts to boil?

**Chemist:** I don't know. My experiments never boiled.

**Engineer:** Why do you always run in a round-bottom flask? You could get faster conversion in a tubular reactor.

**Chemist:** Look, I need to slow the reaction down, not speed it up. When it runs too fast, it makes too much by-product. Then the product goes brown, not white, like it probably should be.

**Engineer:** How can you remove the color?

**Chemist:** I don't know. Sometimes activated carbon works on problems like these.

**Engineer:** Can you try to get any purification when you make the acetone knock-out?

**Chemist:** You mean add the acetone slowly so that you get purer crystals? That's a good direction to go, though it's hard at −40°C. I didn't do it, because I was just trying to rough out the process chemistry.

**Engineer:** Did you measure the purity of that intermediate precipitate?

**Chemist:** No. I don't think it is that important.

**Engineer:** How did you separate the product? The one after hydrolysis.

**Chemist:** Actually I didn't. I just ran the solids that were knocked out and hydrolyzed through the HPLC (high pressure liquid chromatograph). I knew where the peaks should be because of earlier experiments using combinatorial chemistry.

**Engineer:** Do you know how to purify the product?

**Chemist:** Sure.

**Engineer:** I mean at large scale.

**Chemist:** But that's your job. I finished this one, and I did it right. I've got other reactions to run. Come back and see me if you need help. This isn't hard. See you later.

This ended the discussion.

Na osnovi pogovora je kemijski inženir ugotovil sledeče:

- reakcija je močno eksotermna,
- selektivnost reakcije je močno odvisna od temperature,
- reakcijo verjetno kontrolira prenos snovi (hitrost je bila odvisna od mešanja),
- s separacijskimi procesi bo potrebno iz produkta odstraniti nezreagirane reaktante in stranske produkte,
- adsorpcija je primeren separacijski proces (kromatografija je bila primerna za separacijo),
- izbira topila je zelo pomembna, a kemik temu ni namenil pozornosti.

V takšnem primeru mora kemijski inženir preveriti rezultate kemika. Ponoviti mora sintezo na popolnoma enak način in pri tem pridobiti manjkajoče podatke. Beležiti mora, kako se temperatura reakcijske zmesi spreminja s časom. S pomočjo HPLC mora separirati produkt...

Šele, ko ima kemijski inženir na razpolago vse potrebne podatke, se posveti reakcijskemu inženirstvu.

**Reakcijsko inženirstvo**

V tem koraku moramo določiti hitrost in selektivnost kemijskih reakcij. Iščemo korake, ki omejujejo hitrost različnih reakcij (»rate limiting steps«).

Za zgoraj opisani primer bomo določali, kako se koncentracija limitnega reaktanta spreminja s časom. V večini primerov je kot limitni reaktant izbran najdražji reaktant. Včasih pa je, da se izognemo nastanku velikih količin stranskih produktov, potrebno v stehiometričnem prebitku uporabljati najdražji reaktant.

Hitrost kemijske reakcije je lahko kontrolirana s kemijsko kinetiko ali pa s prenosom snovi. Preverili bomo, kako koncentracija limitnega reaktanta vpliva na hitrost reakcije. Na osnovi tega, kako se koncentracija limitnega reaktanta spreminja s časom, bomo določili red reakcije. Če koncentracijo limitnega reaktanta razpolovimo in se pri tem tudi hitrost reakcije razpolovi je reakcija 1. reda, če se hitrost pri tem zmanjša štirikrat, je reakcija 2. reda in če sprememba koncentracije reaktanta na hitrost sploh ne vpliva, je reakcija 0. reda.

Nato je potrebno raziskati, kako je hitrost reakcije odvisna od temperature in mešanja. Za prvo oceno pri identifikaciji koraka, ki omejuje hitrost reakcije si lahko pomagamo s tabelo 6.1-1.

Tabela 6.1-1 (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**TABLE 6.1–1 Identifying the Rate-Limiting Step**

| | Variation with | | | |
|---|---|---|---|---|
| **Limiting Reagent** | **Temperature** | **Stirring** | **Rate-Limiting Step** | **Remarks** |
| First order | Strong | Weak | Chemical kinetics | Most common case |
| | Weak | Strong | Mass transfer | Common for pharmaceuticals |
| Second order | Strong | Weak | Chemical kinetics | Uncommon; if one reagent is in excess, becomes first order |
| Zero order | Varies | Weak | Chemical kinetics | Often indicates catalysis |

*Note:* This brief summary should be used as an introduction, supplemented by books on reaction engineering.

Primeri (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

### EXAMPLE 6.1–1 PENICILLIN MODIFICATION

The addition of a phenyl group to a $\beta$-lactam ring shows the following kinetics:

| time, sec | concentration, $\beta$-lactam |
|---|---|
| 0 | 0.0110 M |
| 200 | 0.0072 |
| 400 | 0.0047 |
| 600 | 0.0032 |

If the $\beta$-lactam is the limiting reagent, what is the reaction order? What is the rate constant?

SOLUTION

A plot of the logarithm of $\beta$-lactam concentration versus time is nearly linear. This is characteristic of a first order reaction. To show why, consider the mass balance

$$[\text{rate of change of } \beta\text{-lactam concentration}] = [\text{reaction rate of } \beta\text{-lactam}],$$
$$V(dc_1/dt) = -kc_1V,$$

where $V$ is the volume of the reactor, $c_1$ is the $\beta$-lactam concentration, $t$ is the time, and $k$ is a first order rate constant. If the initial concentration of the $\beta$-lactam is $c_{10}$, this equation is easily integrated:

$$c_1/c_{10} = c^{-kt}.$$

Thus a plot of $ln\ c_1$ versus $t$ should have a slope of $-k$. In this case, $k$ equals about $2 \times 10^{-3}$ sec$^{-1}$.

### EXAMPLE 6.1–2 ETCHING A PHOTORESIST

Imagine that we are etching a silicon wafer coated with a new optically sensitive photoresist with a dilute solution of aqueous sodium hydroxide. The reaction rate shows an activation energy around 30 kJ/mol, suggesting the reaction may be strongly influenced by chemical kinetics. However, the reaction rate in 0.16 M of NaOH also depends on the spinning speed of the wafer, as shown by the isothermal data below.

| wafer rotation, rpm | rate constant, sec$^{-1}$ |
|---|---|
| 6 | 0.53 |
| 9 | 0.61, 0.61 |
| 15 | 0.70, 0.66 |
| 30 | 0.81, 0.79, 0.88 |
| 70 | 1.16 |

What is the reaction mechanism?

SOLUTION

In many cases, including this one, the rate is affected both by chemical kinetics and by mass transfer. In cases such as these, we may show that the overall reaction rate constant, $k$, is given by

$$\frac{1}{k} = (1/k_{\text{surface}}a) + (1/k_D a),$$

where $k_{\text{surface}}$ is the rate constant for surface reaction, $k_D$ is that for diffusion (i.e., the mass transfer coefficient), and $a$ is the surface area per volume. Because these two reactions occur sequentially, this result is often said to correspond to two chemical resistances in series, and it is compared to Ohm's law of electrical resistances in series.

At constant temperature, we expect $k_{\text{surface}}$ to be a constant, but $k_D$ to vary with stirring. In most cases, $k_D$ varies with stirring speed to the power of 0.3 to 0.8. The most common power is 0.5, which is that for the dissolution as given above. Thus we can expect

$$\frac{1}{k} = (1/k_{\text{surface}}a) + (\text{B}/\omega^{1/2}),$$

where $\omega$ is the speed of rotation and B is a constant. Thus a graph of $(1/k)$ versus $(1/\omega^{1/2})$ should be linear, with an intercept proportional to the chemical rate constant, and a slope related to the diffusion constant. Such a graph, sometimes called a Wilson plot, does work in this case, as shown in Figure 6.1–1.

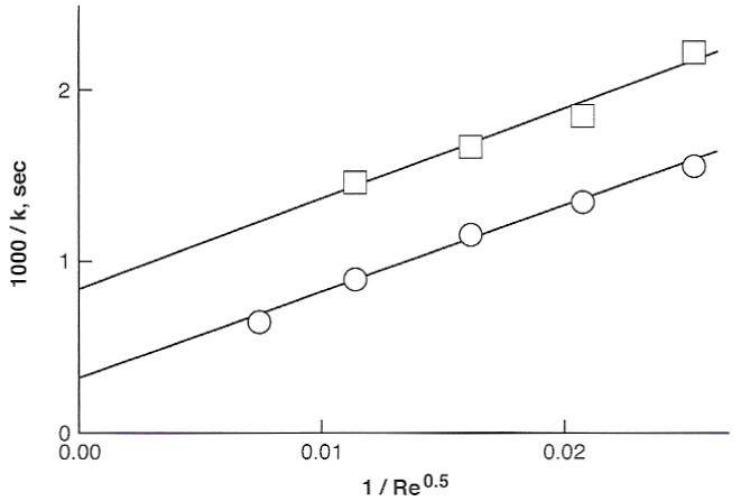



**Figure 6.1–1. Dissolution Rates for a Light-Sensitive Photoresist.** These experimentally determined rates in two different etchants are analyzed as an overall mass transfer coefficient $k$, which is a function of both chemistry and diffusion. In this Wilson plot, values of $k^{-1}$ are plotted vs. the reciprocal of velocity, shown as a square root of Reynolds number Re($=dv/v$). The intercept on the graph is the chemical contribution; the slope is related to the effect of diffusion.

### 6.6.2 Separacije

Pri separacija zmesi visoko razredčenih kemikalij je zelo pomembno zaporedje separacijskih procesov, po katerem bomo separirali posamezne komponente iz zmesi, in izbor konkretne metode separacije. Destilacija, ki se v proizvodnji proizvodnih kemikalij zelo pogosto uporablja, je v primeru kemijskih produktov manjkrat izbrana tehnika.

#### Vrstni red separacijskih procesov

Ker se različni produkti po sintezi med seboj zelo razlikujejo, se razlikujejo tudi njihovo čiščenje s separacijskimi metodami. Spodnja pravila so za specialne kemikalije v večini primerov primerna:

1. Koncentriranje produkta pred čiščenjem. (Najprej iz produkta odstranimo velike količine vode ali topil. Pri tem se ne obremenjujemo s selektivnostjo. Na ta način predvsem zmanjšamo volumen produkta.)
2. Zgodnje odstranjevanje komponente, ki je je največ. (To je še posebej koristno, če lahko komponento prodamo ali uporabimo.)
3. Najbolj zahtevna separacija se izvede zadnja.
4. Zgodnje odstranjevanje nevarnih snovi iz produkta.
5. Med separacijo se je potrebno izogibati uvajanju novih nečistoč v produkt. Če je to nujno, potem jih je potrebno čim prej odstraniti. (Dodajamo topila (ekstrakcija), adsorbente, detergente...)
6. Izogibanje ekstremnim temperaturam. Raje uporabimo različna topila. (Visoke temperature lahko povzročijo razpad produkta, doseganje nizkih temperatur pa je drago.)

Slika 6.2-1: Pomen koncentriranja (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

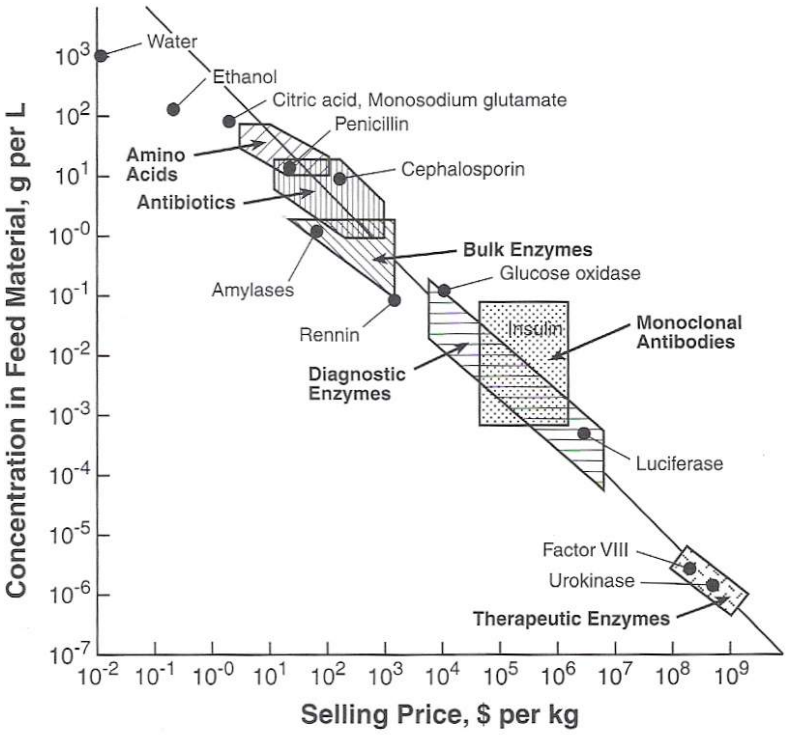



**Figure 6.2–1. Sherwood Plot of Selling Price Against Concentration in Feed Material.** Although this particular plot is for biological products, similar graphs can be produced for other classes of materials.

**Najbolj koristne separacijske tehnike za specialne kemikalije**

Najpomembnejše separacijske tehnike so zbrane v tabeli 6.2-1.

Tabela 6.2-1 (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**TABLE 6.2–1 Key Separation Processes for Specialty Chemical Products**

| Class 1<br>Distillation | Class 2<br>Workhorses Requiring Thought | Class 3<br>Other Important Processes |
|---|---|---|
| Fractional distillation | Extraction | Drying/evaporation |
| Steam distillation | Adsorption<br>(including ion exchange) | Filtration<br>(including ultrafiltration) |
| | Crystallization<br>(including precipitation) | Centrifugation |
| | | Absorption |
| | | Membrane separation |
| | | Electrophoresis |

Frakcionirna destilacija je najpomembnejša separacijska tehnika v kemijski procesni industriji pri proizvodnji proizvodnih kemikalij. Za čiščenje specialnih kemikalij pa ni najbolj primerna, ker je večina specialnih kemikalij slabo hlapnih in slabo temperaturno obstojnih.
Za specialne kemikalije je veliko bolj pomembna destilacija z vodno paro. Primerna je za separacijo v vodi slabo topnih kemikalij, tudi če so te slabo temperaturno obstojne, od nehlapnih nečistoč. Ker imamo dvofazen sistem se temperatura vrelišča zniža. Destilacija z vodno paro je primeren postopek za pridobivanje rastlinskih ekstraktov.

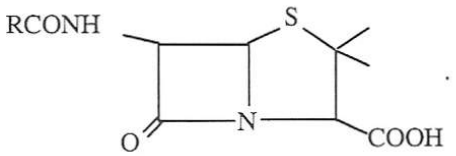
Ekstrakcija, adsorpcija in kristalizacija so za specialne kemikalije najpomembnejše separacijske tehnike. Vse tri se uporabljajo za koncentriranje razredčenih raztopin in narekujejo končno ceno produkta. So selektivne metode. Ko se uporabljajo za čiščenje produkta, so to energijsko zahtevni procesi. Ekstrakcija se uporablja predvsem za koncentriranje produkta, adsorpcija je največkrat glavna tehnika čiščenja produkta, medtem ko se kristalizacija pogosto uporablja za končno (fino) čiščenje produkta.

Zelo pogosto se uporabljata sušenje in filtracija ter pogosto tudi centrifugiranje, absorpcija, membranska separacija in elektroforeza.

Primer (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**EXAMPLE 6.2–1 PENICILLIN PURIFICATION**

This classic process is the model for a huge group of antibiotics, including cephalosporins, which are based on $\beta$-lactams. For the penicillins, the basic structure is



These molecules can be made either chemically or microbiologically. In the microbiological route, mutants of *Penicillium chrysogenum* are grown in 100,000-L aerated fermenters that are charged primarily with lactose, corn steep liquor, and

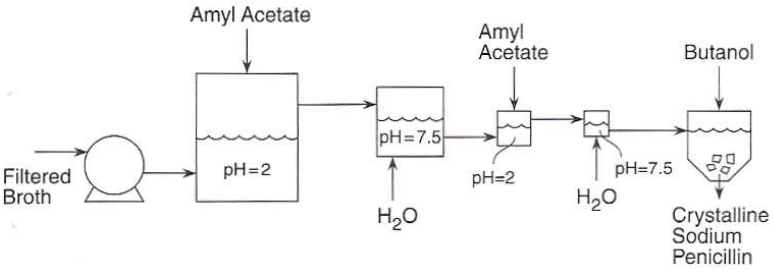



**Figure 6.2–6. A Schematic Process for Penicillin Purification.** Aqueous pencillin at pH 2 is extracted into amyl acetate and then backextracted into water at pH 7.5. After this process is repeated, the product is crystallized from a water-butanol mixture.

calcium carbonate. After about 7 days, the broth contains perhaps 80 mg of penicillin per liter of broth.

Suggest how the penicillin can be isolated and purified.

SOLUTION

The key to this purification is the recognition that these materials are carboxylic acids. When the pH is above about 5.5, the COOH group ionizes to $COO^-$ and the penicillin becomes water soluble. When the pH is below 5, the COOH group remains protonated, and the penicillin is more soluble in organic extraction solvents.

Hence, the purifications used for penicillin rely heavily on extraction. A typical process is shown in Figure 6.2–6. This first step is to separate the penicillin containing broth from the large biomass of micro-organisms. Because normal filters tend to plug, this separation often involves adsorption of the microbes on diamataceous earth (Filter-Aid) and then filtration. The clarified broth is acidified and then extracted with amyl acetate. Because the acid form of the penicillin is less stable, this extraction should be as fast as possible. Then the amyl acetate is extracted with water at pH 7.5, so the product moves back into the water. This entire process is repeated until the penicillin is concentrated perhaps 100 times. Finally, butanol is added to the aqueous penicillin solution to precipitate crystals of sodium or potassium penicillin.

This process is a simplification of what is actually done. In fact, the first amyl acetate extract is decolorized by adsorption on activated carbon. The last aqueous extract may be dried as a crude product before it is redissolved and crystallized. Still, this purification is an excellent example because it depends on recognizing one key chemical fact: penicillin is a carboxylic acid.

### 6.6.3 Povečevalni kriteriji ("scale-up")

Vemo kakšno kemikalijo bomo naredili, kako jo bomo naredili in kako jo bomo očistili. Sedaj je potrebno narediti večje količine čiste kemikalije. V ta namen proces sinteze in separacije povečujemo (»scale-up«).
Povečevanje, ki se uporablja za specialne kemikalije, se bistveno razlikuje od povečevanja procesov in naprav za proizvodne kemikalije. Glavni cilj povečevanja, ki se uporablja za proizvodne kemikalije je, da na industrijskem nivoju postavimo naprave in procese, ki smo jih predhodno, posebej za namen učinkovite izdelave specifične proizvodne kemikalije, razvili v laboratoriju. Na industrijskem nivoju želimo izdelati produkt enake ali boljše kvalitete po enakih optimiziranih postopkih kot v laboratoriju (oziroma pilotnih napravah).

Ko na industrijskem nivoju postavljamo sintezo in separacije za proizvodnjo specialnih kemikalij, uporabljamo generične reaktorje in separatorje, ki jih imamo na razpolago (smo jih že uporabljali za druge namene in jih bomo tudi v prihodnosti uporabljali še za druge namene). Produkt želimo narediti na obstoječih napravah.

Za farmacevtsko industrijo je značilno, da se laboratorijske in industrijske naprave (razen po velikosti) zelo malo razlikujejo. To pa zato, ker so materiali, na katerih se opravljajo klinični poskusi, izdelani na laboratorijskih napravah. Če so rezultati kliničnih poskusov pozitivni in so izpolnjene vse potrebne zahteve, se odobrita material in proces izdelave. Sprememba procesa (zamenjava vrste reaktorja, separatorja, topila...) zahteva ponoven postopek za odobritev. Ker so to dolgotrajni in dragi postopki, se jim bomo poskušali izogniti tako, da bo industrijski proces čim bolj podoben laboratorijskemu.

Pri povečevanju specialnih produktov želimo, da ostanejo procesne spremenljivke v enakem razmerju kot v laboratorijskem merilu. Želimo enake hitrostne konstante, prenos toplote, porazdelitvene faktorje...

Včasih, če je to smiselno, namesto »scale-up« pristopa uporabljamo »numbering-up«. Namesto, da napravo povečamo, postavimo na industrijski liniji več enakih naprav, katerih velikost je enaka velikosti laboratorijske naprave.

#### Povečevanje reaktorjev

Povečevanje kemijskih reaktorjev zajema kontrolo kemijske kinetike, kontrolo prenosa snovi in kontrolo prenosa toplote.

Ko so reakcije kontrolirane s kemijsko kinetiko, je povečevanje najlažje. Za reakcijo prvega reda v šaržnem reaktorju je koncentracija reaktanta 1 ($c_1$):

$$c_1 = c_{10} \cdot e^{-kt}$$

kjer je $c_{10}$ začetna koncentracija reaktanta 1, k konstanta reakcijske hitrosti in t čas. Če je temperatura konstantna, ni nič odvisno od velikosti reaktorja. Vseeno je ali vzamemo 100 krat večji reaktor ali pa 100 laboratorijskih reaktorjev.

Ko so reakcije kontrolirane s prenosom snovi je:

$$c_1 = c_{10} \cdot e^{-k_D at}$$

kjer je $k_D$ snovna prestopnost in a površina reaktanta na volumen. Če želimo povečevati, mora biti $k_Da$ konstanten. $k_Da$ pa je odvisen od velikosti reaktorja. Kakšna je odvisnost $k_Da$ od velikosti reaktorja je odvisno od primera do primera.

- Primer 1: Prezračevanje mešalnega reaktorja. Iz eksperimentov vemo, da je $k_Da = f(P/V, v_g)$, kjer je P/V volumski vnos moči in $v_g$ hitrost zraka (volumski pretok zraka skozi presek reaktorja). Reaktor bomo povečevali tako, da bosta P/V in $v_g$ enaka kot na laboratorijskem reaktorju. Industrijski reaktor bo imel enako geometrijo kot laboratorijski reaktor.

- Primer 2: Počasno dodajanje limitnega reaktanta v ohlajeno raztopino prebitnega reaktanta. Volumen v reaktorju se ne spreminja. Hitrost procesa je kontrolirana s hitrostjo mešanja (s prenosom snovi). Proces je prvega reda in ga opiše zgornja enačba.
  Da bo razmerje $c_1/c_{10}$ v industrijskem reaktorju enako tistemu v laboratorijskemu, mora biti čas mešanja:

  čas mešanja $\propto \frac{1}{k_D a} \propto \frac{l^2}{D}$

  kjer je l velikost vrtinca in D difuzivnost.

  $$l \propto \left(\frac{\rho \nu^3}{P/V}\right)^{0,25}$$

  kjer je $\rho$ gostota produkta, $\nu$ kinematična viskoznost produkta ter P/V vnos moči na volumen v mešalniku. Torej:

  $$k_D a \propto D \left(\frac{P/V}{\rho \nu^3}\right)^{0,5}$$

  Snovne lastnosti (difuzivnost, gostota in kinematična viskoznost) bodo enake na laboratorijskem in industrijskem reaktorju, zato povečujemo glede na volumski vnos moči.

Veliko kemijskih reakcij je eksotermnih. Da reakcijo vodimo pri želeni temperaturi, je potrebno iz reaktorja odvajati toploto. Odvajanje toplote iz večjih reaktorjev je težje, ker je njihovo razmerje med površino (preko katere toploto odvajamo) in volumnom manjše. Količina toplote, ki jo lahko odvedemo je odvisna od površine reaktorja, medtem ko je količina sproščene toplote med kemijsko reakcijo odvisna od volumna reaktorja. V večini primerov, ko imamo takšne težave, moramo spremeniti način odvajanja toplote. S pomočjo zapisa energetske bilance za aidiabatni reaktor z eksotermno reakcijo, v katerem temperatura v času t naraste od $T_0$ na $T_R$, dobimo, da moramo reaktor hladiti po enačbi:

$$\frac{T - T_0}{T_R - T_0} = \exp(-\frac{UAt}{\rho C_p})$$

kjer je U toplotna prehodnost, A specifična površina, $\rho$ gostota produkta in $C_p$ specifična toplota produkta. Snovne lastnosti bodo enake na laboratorijskem in industrijskem reaktorju. Sprememba A bi pomenila spremembo geometrije reaktorja. Lahko povečamo U za industrijski reaktor. Lahko znižamo tlak v reaktorju, da bo vsebina vrela.

**Povečevanje separatorjev**

Povečevanje različnih separacijskih procesov je zelo različno. Povečevanje ekstrakcije je dokaj enostavno (porazdelitevni koeficienti so enaki na laboratorijski in industrijski napravi, ohranjamo razmerje med pretokom topila in napajalne zmesi). Povečevanje adsorpcije je veliko bolj zahtevno in zahteva sprejemanje kompromisov (lahko spremenimo višino kolone, premer kolone, velikost delcev v nasutem sloju, hitrost fluida, padec tlaka na koloni...). Povečevanje kristalizacije pa je izredno kompleksno (težko je zagotoviti popolnoma enako hlajenje na industrijski napravi kot v laboratoriju, površina večjih kristalizatorjev na volumen je manjša (stena je hladnejša od glavnine prenasičene raztopine), imamo različne nukleacijske mehanizme (heterogena nukleacija, homogena nukleacija, sekundarna nukleacija), vpliv mešanja...).

Primeri (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**EXAMPLE 6.3–1 REACTING SUSPENDED STEROIDS**

You are reacting a suspension of steroid particles, about 2.60 $\mu$m in diameter, with butyl lithium in tetrahydrofuran at $-20^{\circ}$C. You believe that the reaction is mass transfer controlled, with the mass transfer coefficient $k_D$ given by the correlation (Boon-Jong et al., 1978)

$$k_D d/D = 0.46(dd'\omega/\upsilon)^{0.28}(gd^3/\upsilon^2)^{0.17}(M_T/\rho d^3)^{-0.011}(d'/d)^{0.02}(\upsilon/D)^{0.46},$$

where $d$ is the particle diameter; $D$ is the reagent diffusion coefficient in the liquid; $d'$ and $\omega$ are impeller diameter and speed, respectively; $\upsilon$ and $\rho$ are the kinematic viscosity and density of the liquid, respectively; $g$ is the acceleration that is due to gravity; and $M_T$ is the particle mass.

You want to scale up the reaction 1000 times using the same size particles. How should you proceed?

SOLUTION

This is a good example of a problem with extraneous information. If you look at the correlation, you see that the only variables you can control are $d'$ and $\omega$. But

$$k_D \propto (d'\omega)^{0.28}(d')^{0.02}.$$

If we are scaling up 1000 times with a geometrically similar reactor, then $d'$ increases ten times. Thus to keep $k_D$ the same, we should decrease $\omega$ about eight times. This is close to scaling at constant Reynolds number $(dd'\omega/\upsilon)$.

**EXAMPLE 6.3–2 SCALING UP A LINCOMYCIN ADSORPTION**

We are adsorbing both lincomycin A and B from a clarified fermentation beer onto a modified dextran resin. The resin, which can stand pressure drops up to 1000 kPa, shows a highly favorable isotherm for these products. In the laboratory, we have run the beads in a 1.6-cm-diameter tube packed to a depth of 34 cm. With a pressure drop of only 60 kPa, we get a lincomycin breakthrough at 46 min, and an exhausted bed at 62 min.

We want to run this system in an existing pilot plant adsorption bed that is 30 cm in diameter. We have already operated this bed by using a pressure drop of 410 kPa. How much can we scale up this process? How should we operate to scale up a factor of 5000 times?

SOLUTION

To begin, imagine that we operate the 30-cm-diameter bed under exactly the same conditions as the laboratory bed. Because the pressure drop and the bed length are unchanged, the velocity, the breakthrough time, and the exhaustion time are all the same. Thus the gain in capacity is solely due to the gain in the relative cross sectional areas:

$$[\text{gain in scale up}] = \left[\frac{\text{cross section of pilot bed}}{\text{cross section of laboratory bed}}\right]$$

$$\frac{\pi/4(30\text{ cm})^2}{\pi/4(1.6\text{ cm})^2} = 350.$$

This reasonable increase is smaller than we seek.

As a second alternative, we can operate at the same velocity but in a deeper bed. In the laboratory, we got satisfactory results in a bed 34 cm deep, using a pressure drop of 60 kPa. Because we know that we can increase the pressure drop to 410 kPa, we can use a deeper bed:

$$[\text{pilot bed depth}] = [\text{laboratory bed depth of 34 cm}]\frac{410\text{ kPa}}{60\text{ kPa}} = 230\text{ cm}.$$

Because the isotherm is favorable, the length of unused bed is constant. For the laboratory bed, the length of unused bed $l'$ is just

$$l' = l\left(\frac{t_E - t_B}{2t_B}\right),$$

$$= 34\text{ cm}\left[\frac{62\text{ min} - 46\text{ min}}{2(46\text{ min})}\right] = 6\text{ cm}.$$

Thus the increased capacity is now

$$\text{gain in scale up} = \frac{\text{volume used in pilot bed}}{\text{volume used in laboratory bed}},$$

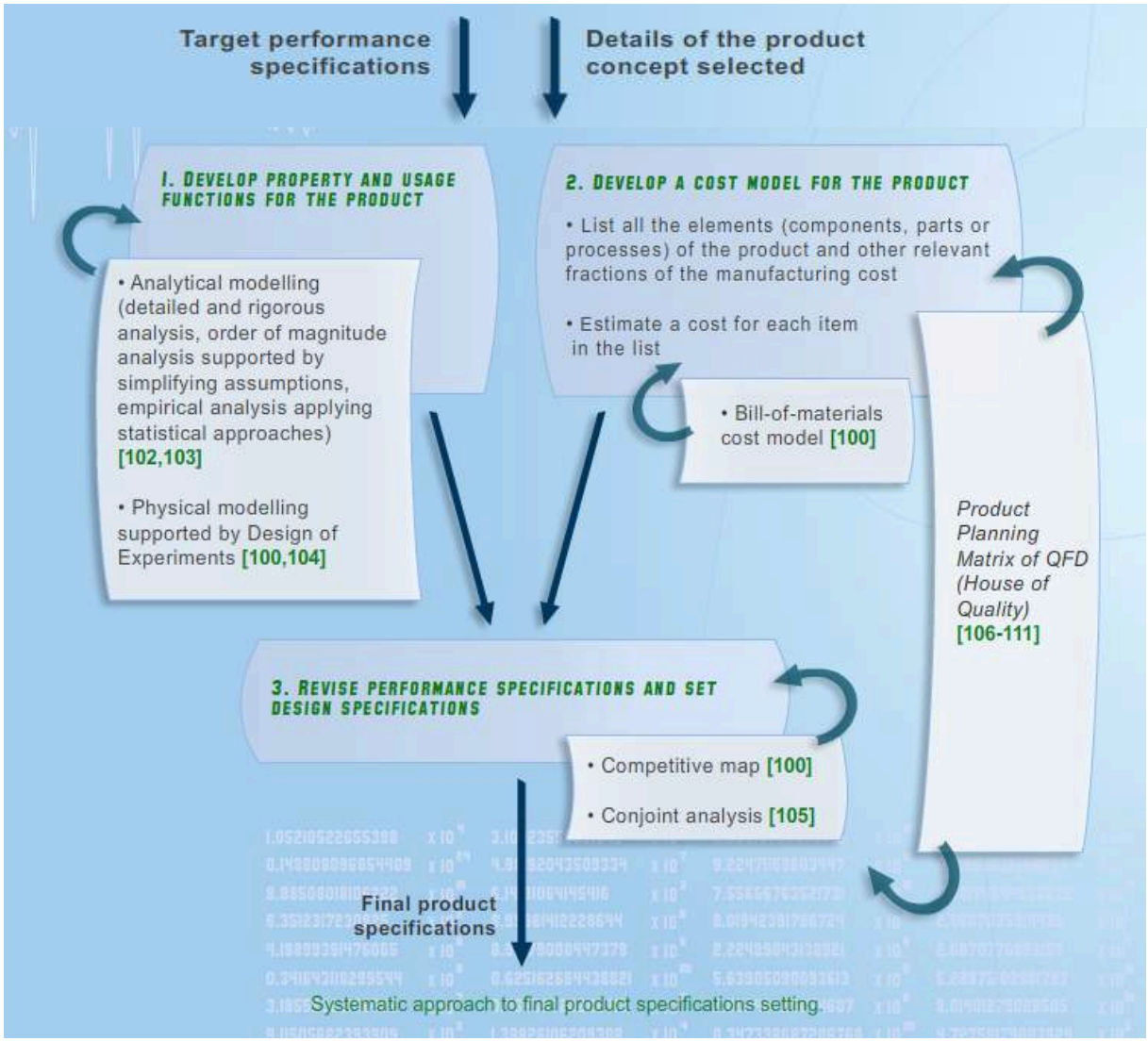
$$= \frac{\pi/4(30\text{ cm})^2(230\text{ cm} - 6\text{ cm})}{\pi/4(1.6\text{ cm})^2(34\text{ cm} - 6\text{ cm})},$$

$$= 2800.$$

This is a substantial increase, but still less than the factor of 5000 we had hoped for.

To go still higher, we will need to take risks tempered by additional experiments. If possible, we still want to use the same bed velocity. Because the adsorbent is said to stand a pressure drop of 1000 kPa, we could investigate running at the same velocity in a still deeper bed. To do so, we must make sure that our pilot column can also stand the higher pressure. Alternatively, we can increase the adsorbent diameter and hence the velocity through the bed. Doing so will almost certainly increase the length of unused bed, perhaps dramatically. Before we make this more radical change, we will need more laboratory experiments using bigger velocities past bigger particles.

Shematski prikaz : Določitev končnih specifikacij
*Vir: http://www.engsc.ac.uk/an/mini_projects/cpd/index.html (6.9.2011)*




Primera določanja končnih specifikacij: Parfum
*Vir: http://www.engsc.ac.uk/an/mini_projects/cpd/index.html (6.9.2011)*

# 8 EKONOMIJA NOVEGA PRODUKTA

## 8.1 Primerjava načrtovanja procesov in produktov

Produkt procesne industrije je proizvodna kemikalija, produktne pa kemijski produkt. Najlažje je primerjati proizvodne kemikalije s specialnimi kemikalijami, ki so tipičen predstavnik kemijskih produktov.

Proizvodne kemikalije:
1. *Koliko se jih proizvede?* Več kot 10 000 ton letno.
2. *Kakšno opremo potrebujemo?* Specifično opremo za določeno kemikalijo. Proces je kontinuiren.
3. *Kateri proizvajalec ima največji dobiček?* Tisti, ki ima najnižje stroške proizvodnje.

Specialne kemikalije:
1. *Koliko se jih proizvede?* Manj kot 10 ton letno.
2. *Kakšno opremo potrebujemo?* Generično opremo. Proces je navadno šaržen.
3. *Kateri proizvajalec ima največji dobiček?* Tisti, ki je najprej z novim izdelkom na tržišču (70 % trga).

## 8.2 Ekonomika procesa

Proizvajalec proizvodne kemikalije ve, kakšna bo prodajna cena produkta na trgu (enaka tisti, ki jo ima konkurenca). Zato želi kemikalijo proizvesti na najcenejši način in govorimo o ekonomiki procesa.

Ekonomija kemijskega procesa je odvisna od:

1. izbire procesa sinteze: šaržni ali kontinuirni,
2. procesnih tokov (vstopi, izstopi),
3. reakcij, konverzij, reciklov,
4. izbire separacijskih procesov in integracije energije.

Preverimo ali je ekonomski potencial za proces pozitiven. To naredimo v treh zaporednih korakih:

1. [ekonomski potencial (prva ocena)] = [letni prihodek od prodaje produkta] - [letni stroški surovin]
2. [ekonomski potencial (druga ocena)] = [letni prihodek od prodaje produkta] - [letni stroški surovin] – [letni obratovalni stroški]
3. [ekonomski potencial (tretja ocena)] = [letni prihodek od prodaje produkta] - [letni stroški surovin] – [letni obratovalni stroški] – [letni skupni stroški kapitala]

Na sliki 7.2-1 je prikazana osnovna shema za izračun letnih skupnih stroškov kapitala.

Slika 7.2-1 (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

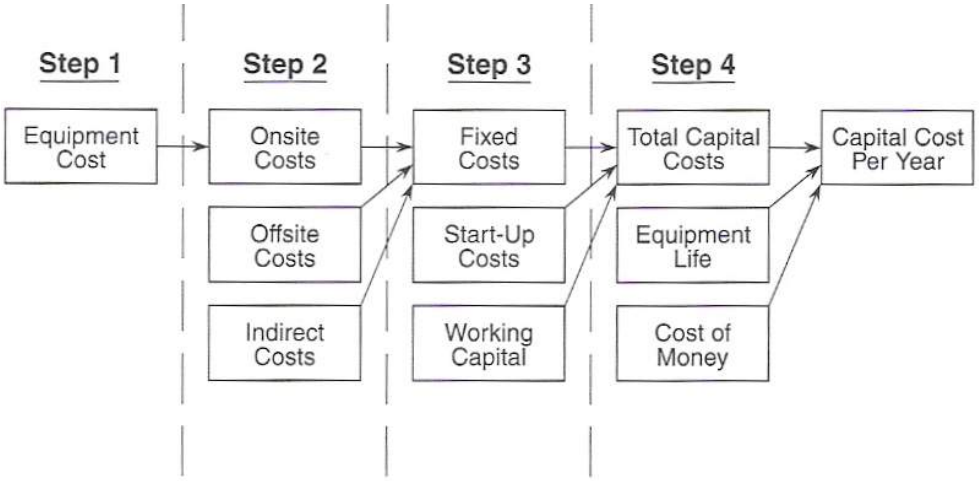



**Figure 7.2–4. Estimating the Yearly Capital Cost.** Knowing this quantity is the last step in estimating the economic potential of a commodity chemical process.

Stroške procesne opreme ocenimo na osnovi cen različnih kosov opreme pri prodajalcih opreme.

Stroški gradnje proizvodne linije (»Onsite costs«)so navadno višji od stroškov opreme (okoli 4 krat). Stroški za generacijo energije in gradnjo pomožnih objektov (»Offsite costs«) navadno predstavljajo okoli 45 % stroškov gradnje proizvodne linije.
Indirektni stroški so stroški notranjega (našega) inženiringa znašajo okoli 25 % stroškov vseh gradenj.

Fiksni stroški so tako okoli 7.2 krat večji kot stroški procesne opreme.
Stroški zagona so stroški inženiringa in dela, ki so potrebni za zagon proizvodnje (okoli 10 % fiksnih stroškov).
Delovni kapital vključuje stroške, ki smo jih imeli za surovine, iz katerih smo že naredili produkt, a ga še nismo prodali (okoli 15 % totalnih stroškov kapitala).

Totalni stroški kapitala so okoli 1,3 krat večji kot fiksni stroški in 9.4 krat večji kot stroški procesne opreme.
S pomočjo življenjske dobe opreme in stroškov denarja (obrestna mera) dobimo letne stroške kapitala. Če bi bila življenjska doba opreme 10 let in stroški denarja 15 %, bi bili letni stroški kapitala 4 krat večji kot stroški procesne opreme.

Ko ocenjujemo ekonomijo procesa predpostavljamo, da bodo imeli izdelki dolgo življenjsko dobo.

### 8.3 Ekonomika produkta

Ko razvijamo nov produkt, trga še ni, prav tako ni določena cena produkta na trgu. Ker je življenjska doba kemijskih produktov na trgu relativno kratka, moramo imeti dovolj velik dobiček od prodaje produkta v kratkem času (5-10 let).

Ekonomika kemijskega produkta je temelji na neto sedanji vrednosti, na času, od začetka investicije do prodaje produkta na trgu - "time to market" in na časovni vrednosti denarja.

Neto sedanja vrednost produkta je sedanja vrednost produkta v evrih ob upoštevanju bodočih denarnih tokov.

Definicija neto sedanje vrednosti. Vir: http://www.akc.si/investicije.php:

> "Neto sedanjo vrednost – NSV lahko opredelimo kot razliko med diskontiranim tokom vseh prilivov in dikontiranim tokom vseh odlivov neke naložbe ali kot vsoto diskontiranih neto prilivov iz finančnega toka naložbe. Po tej metodi torej diskontiramo prihodnje donose in investicijske izdatke na začetni termin ko nastopijo prvi investicijski izdatki. Zaradi časovne vrednosti denarja nima 1 tolar, ki ga prinaša naložba v bodoče, tako velike sedanje vrednosti kot 1 tolar danes. Pozitivna NSV pomeni znesek za katerega je sedanja vrednost pozitivnega toka koristi večja od sedanje vrednosti celotnega negativnega toka stroškov, oziroma, da je razlika med vrednostjo proizvedenega ali ohranjenega bogastva in vrednostjo porabljenih sredstev pozitivna.
>
> Pravilo za odločitev o naložbi na osnovi NSV je, da naložbo sprejmemo, če je NSV večja od 0 (nič) in jo zavrnemo, če je NSV manjša od 0 (nič). Če je NSV enaka nič, smo pri odločitvi ravnodušni. Med več alternativnimi investicijskimi možnostmi pa izberemo tisto, ki ima najvišjo pozitivno NSV. Naložba je namreč sprejemljiva le tedaj, ko ni druge alternativne naložbe, ki bi pri enakih investicijskih stroških dajala višjo vrednost donosov.
>
> Tudi NSV ni vsesplošno uporabna, saj NSV ni primerljiva pri dveh investicijah z različno življenjsko dobo ter v primeru ko dve investiciji zahtevata različni nivo stroškov. Ko imata dve investiciji enako življenjsko dobo, a različne stroške, zato lahko uporabimo Indeks donosnosti, kjer namesto razlike med sedanjo vrednostjo donosov in sedanjo vrednostjo stroškov izračunamo razmerje med obema. Investicija je sprejemljiva, če je indeks donosnosti večji od 1 (ena). Izberemo pa tisto investicijo, ki ima večji indeks donosnosti (seveda večji od 1). Ko pa nastopi še razlika v življenjski dobi investicije, izračunamo Ekvivalentni letni donos tako,da izračunamo letno anuiteto oziroma rento, ki bi nam jo omogočila izračunana NSV ob koncu vsakega leta skozi celotno življenjsko dobo pri določeni obrestni meri. S tem pokazateljem so investicije neposredno primerljive tudi če zahtevajo različne investicijske stroške in imajo različne življenjske dobe.
>
> Pri izračunavanju NSV in drugih izvedenih pokazateljev uspešnosti investicij smo videli, da vidno vlogo igra individualna diskontna stopnja, s katero diskontiramo bodoče neto donose. Glede na to, da je uporaba sredstev vedno alternativna, morajo finančna sredstva porabljena za investicijo prinašati najmanj toliko kot v vsaki drugi uporabi. Zato naj bi bila višina individualne diskontne stopnje vsaj približno enaka obrestni meri za kredite, ki jih moramo najeti za financiranje investicije, ali višini donosnosti lastnih finančnih sredstev, ki jo lahko dosežemo s katerokoli drugo alternativno naložbo (oportunitetni strošek), oziroma ponderirana aritmetična sredina obeh, če financiramo investicijo kombinirano z lastnimi sredstvi in kreditom."

Na sliki 7.3-1 je Gantt-ov diagram, ki prikazuje vključenost posameznih sektorjev podjetja (ne projektnega team-a) v štiri letni cikel nekega kemijskega produkta. Projektni team je aktiven okoli leto in pol.

Slika 7.3-1 (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

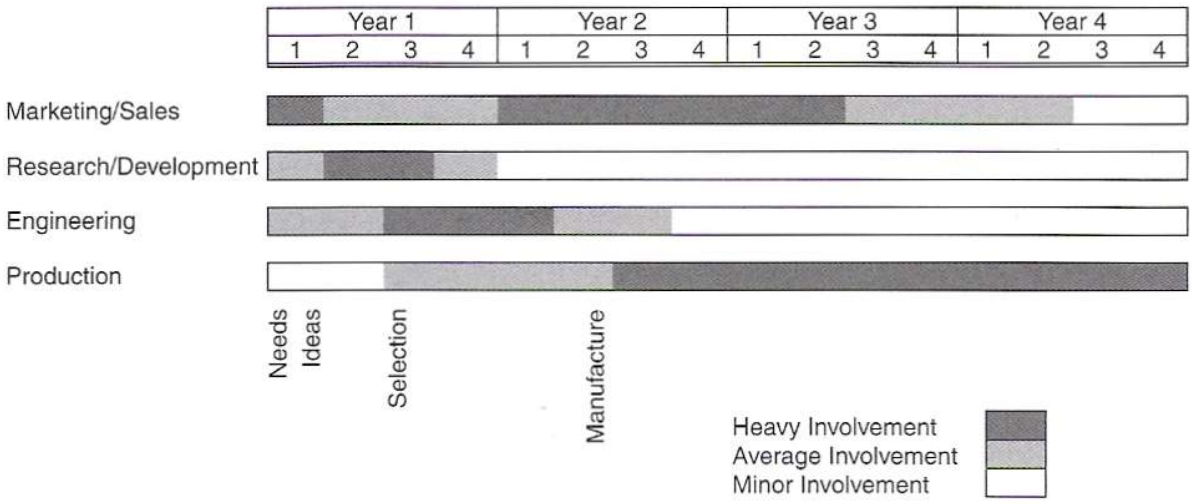



**Figure 7.3–1. Gantt Chart Showing Project Involvement.** The primary responsibility begins with marketing and then moves in turn to research, engineering, and production. Under the project system, however, all groups remain involved through the core team.

**Tok denarja brez upoštevanja časovne vrednosti denarja**

V tabeli 7.3-1 je prikazan primer za štiri letni cikel nekega kemijskega produkta.

Tabela 7.3-1 (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**TABLE 7.3–1 Cash Flow Without the Time Value of Money**

| | Year 1 | | | | Year 2 | | | | Year 3 | | | | Year 4 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Parameter** | **1** | **2** | **3** | **4** | **1** | **2** | **3** | **4** | **1** | **2** | **3** | **4** | **1** | **2** | **3** | **4** |
| Development | −0.69 | −0.69 | −0.69 | −0.69 | | | | | | | | | | | | |
| Equipment | | | −1.00 | −1.00 | | | | | | | | | | | | |
| Start-up | | | | −0.20 | −0.20 | | | | | | | | | | | |
| Production | | | | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | |
| Revenue | | | | | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Cash Flow | −0.69 | −0.69 | −1.69 | −2.89 | 0.80 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 2.00 |
| Net Cash Flow | −0.69 | −1.38 | −3.07 | −5.96 | −5.16 | −4.16 | −3.16 | −2.16 | −1.16 | −0.16 | 0.84 | 1.84 | 2.84 | 3.84 | 4.84 | 6.84 |

*Note:* All values are in $10^6$. Note the time value to break even is in the third year and the return on investment is (\$6.84/5.16/4) = 33%.

**Tok denarja z upoštevanjem časovne vrednosti denarja**

V tabeli 7.3-2 je prikazan primer štiri letni cikel nekega kemijskega produkta.

$$[Tok\ denarja] = \frac{[sedanja\ vrednost]}{\left[1 + \frac{letna\ obrestna\ mera}{4\ \check{c}etrtletja}\right]^{n-1}}$$

Tabela 7.3-2 (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

**TABLE 7.3–2 Cash Flow Including the Time Value of Money[a]**

| | Year 1 | | | | Year 2 | | | | Year 3 | | | | Year 4 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Parameter** | **1** | **2** | **3** | **4** | **1** | **2** | **3** | **4** | **1** | **2** | **3** | **4** | **1** | **2** | **3** | **4** |
| Development | −0.69 | −0.69 | −0.69 | −0.69 | | | | | | | | | | | | |
| Equipment | | | −1.00 | −1.00 | | | | | | | | | | | | |
| Start-up | | | | −0.20 | −0.20 | | | | | | | | | | | |
| Production | | | | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | −1.00 | |
| Revenue | | | | | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Cash Flow | −0.69 | −0.69 | −1.69 | −2.89 | 0.80 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 2.00 |
| Product Value[b] | −0.69 | −0.67 | −1.57 | −2.59 | 0.69 | 0.83 | 0.80 | 0.77 | 0.74 | 0.72 | 0.69 | 0.67 | 0.64 | 0.62 | 0.60 | 1.15 |
| Net Value[b] | −0.69 | −1.36 | −2.93 | −5.51 | −4.82 | −3.99 | −3.19 | −2.42 | −1.67 | −0.95 | −0.26 | 0.41 | 1.05 | 1.67 | 2.27 | 3.42 |

[a]As in Table 7.3–1, all values are in $10^6$. The difference between this and the earlier table is that cash flow is adjusted for 15% interest. The time to break even is a quarter longer, and the net present value drops 50% from $6.84 million to $3.42 million.
[b]Based on the first quarter of Year 1.

**»Time to market«**

Zgornji denarni tokovi ne upoštevajo časa, ki je potreben od začetka projekta do trženja produkta. Ta čas je za kemijske produkte ključen. Proizvajalec, ki pride prvi na trg z novim produktom si lahko obeta, do bo vir njegovega dobička okoli 70 % celotnega tržišča.

Primer (Vir: E. L. Cussler in G. D. Moggridge, Chemical Product Design, Cambridge University Press, Cambridge, 2001.)

### EXAMPLE 7.3–1 THE ECONOMICS OF SCOTTISH MUSSEL FARMING

Mussels are farmed on vertically suspended ropes in Scottish lochs. One problem for mussel farmers is that tube worms settle on the mussel shells and leave a hard, calcinaceous deposit. Although they leave the quality of the mussel meat unaffected, the worm casts are considered unappealing by consumers and in particular restaurants, which account for a significant fraction of mussel sales. Farmers are forced to manually sort and discard seriously fouled mussels to maintain the product quality. Typically 5–25% of the mussel crop is lost in this way.

One idea for mitigating this loss comes from the nature of Scottish lochs, which are narrow fingers of sea water reaching inland. Although the bulk of the water is salty, a significant quantity of fresh water flows into the lochs. Because of its density difference, the fresh water floats, resulting in a salt depleted surface layer of 1 m depth. It turns out that tube worms are less tolerant to fresh water than mussels. It should therefore be possible to discourage tube worm settlement and growth by periodically raising the mussel ropes into the top 1 m of water. We plan to do this by pulling the vertical ropes into a near horizontal position, as shown in Figure 7.3–2.

Investigate the economic viability of this project.

SOLUTION

In current practice, mussel harvest ropes are 7 m long and 30 cm apart, hanging from long horizontal header ropes. We will modify the current network of ropes in a mussel farm by attaching nylon ropes (which run parallel to the main header rope) to the ends of the dangling harvest ropes, thus easing the process of raising a number of these ropes into the required horizontal position. We decide on the

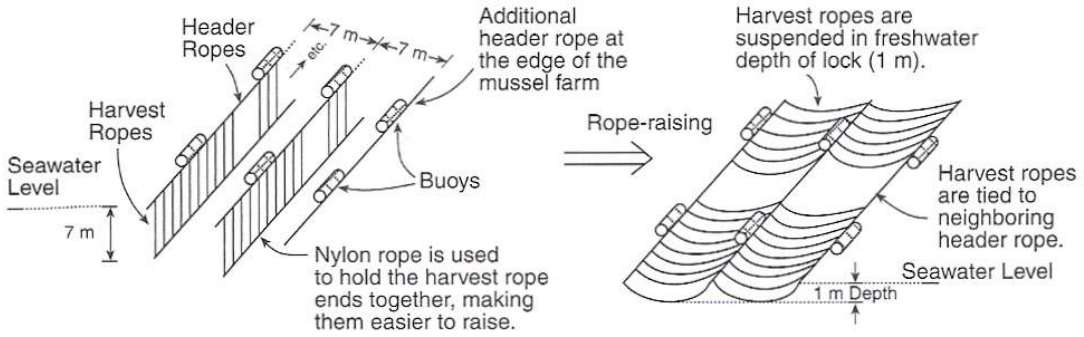



**Figure 7.3–2. Mussel Harvest Ropes.** As explained in the text, these ropes allow raising the mussels from salt water into fresh water, thus reducing the tube worms attached to the mussel shells.

following specifications:

1. Harvest ropes are grouped in batches of ten.
2. Nylon ropes of 32 mm diameter and 3 m length will be tied to the ends of ten harvest ropes to form a sideways ladder "header" rope.
3. The header ropes will be anchored such that they run parallel at an approximate distance apart of 7 m. An extra header rope (with no harvest ropes attached to it) will run parallel to the others at the edge of the mussel field to accommodate the harvest ropes.

A typical mussel farm has 15,000 harvest ropes, producing 150 tons of mussels annually, which sell for £810 per ton. We require 3 m extra rope per ten harvest ropes (i.e., 4500 m additional rope in total) to implement our solution. Because 200 m of 32-mm nylon rope costs £550, we will have a cost of extra rope of £24,750. The ropes will need to be raised every two weeks for a couple of days during the tubeworm breeding season (May to August). This takes about 32 man days of labor, or around £3200 per year. (Casual labor is cheap in Scotland.)

A pilot study shows that raising the ropes achieves a 10% increase in mussel yield per year. This gives an increase in income of $150 \times 0.1 \times$ £810 or £12,150 per year. Finally, we expect that the ropes will need replacing after 5 years.

We are now in a position to calculate the net present value of the project over its 5-year life cycle. We assume that the cost of money is 8% per year. To begin, we see that

$$\text{Net income gain per year} = £12{,}150 - 3200 = £8950.$$

Though capital is spent at the start, income is gained in each of the successive five years, before the ropes must be renewed. Thus

$$\begin{aligned}\text{Net present value} &= -24{,}750 + \frac{8950}{1.08} + \frac{8950}{1.08^2} + \frac{8950}{1.08^3} + \frac{8950}{1.08^4} + \frac{8950}{1.08^5}. \\ &= £10{,}985.\end{aligned}$$

We expect the investment to pay off, with a healthy return on investment of over 40%. The profit will be affected by factors such as the increased yield of mussels and the labor required to raise the ropes.