

### 3 POTREBE

Načrtovanje kemijskih produktov se začne z identifikacijo potreb uporabnika in kupca (potrošnik ali velika korporacija).

Potrebno je:

- ugotoviti, kdo so potencialni uporabniki novega produkta,
- najti načine, kako identificirati potrebe uporabnika,
- najti načine, kako kvantitativno oceniti potrebe potrošnikov (potrošniki svoje potrebe pogosto opisujejo kvalitativno in subjektivno),
- najti načine, kako različne potrebe primerjati med seboj po pomembnosti ter
- na osnovi identificiranih potreb definirati specifikacije, katerim mora ustrezati nov produkt.
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Postavljanje specifikacij produkta zahteva večkratno revizijo, ponovno ocenjevanje in popraviljanje. Navadno se pri tem uporablja referenčni produkt (ang.: benchmark), ki ga želimo zamenjati na trgu (npr.: naš obstoječi produkt ali produkt konkurenčnega proizvajalca).

Identificiramo lahko potrebe za izboljššan produkt ali nov produkt.

Uporabniki so lahko obstoječi uporabniki produkta, ki ga želimo izboljšati, ali pa novi uporabniki.

Izboljššan ali nov produkt lahko zahteva trg ("market-pulled" razvoj).

Lahko priložnost za razvoj novega produkta nudijo inovacije in nove tehnologije ("technology-push" razvoj).

#### 3.1 POTREBE UPORABNIKA

Identificiranje potreb vključuje tri zaporedne korake:

- intervju uporabnika,
- interpretacija izraženih potreb,
- prevedba potreb v specifikacije produkta.

V tej fazi je zelo pomembno, da smo potrpežljivi in ne podajamo rešitev (na osnovi lastnih razmišljanj in razmišljanj kolegov) za nove produkte prehitro, kajti poznavanje uporabnika produkta in njegovih potreb je zelo pomembno.

##### Intervju uporabnika

Glavni vir pri identificiranju potreb so končni uporabniki produkta. Končni uporabniki kemijskega produkta so tisti, ki koristijo (kemijske) lastnosti produkta. Ni nujno, da so končni uporabniki tudi naši kupci. Uporabniki so lahko fizične ali pravne osebe (profitne organizacije, javni zavodi, ...).

"Vodilni uporabniki" (ang.: lead users) zahtevajo posebno pozornost. Le-ti so zelo pomemben vir informacij, saj (naš ali konkurenčen) produkt zelo pogosto uporabljajo in so od njega odvisni. Njihove potrebe zahtevnejše kot potrebe glavnine trga. Vodilni uporabniki, zaradi njihovega znanja in izkušenosti pri uporabi produkta, znajo jasno izraziti slabosti obstoječega (starega, konkurenčnega) produkta. Nemalokrat sami predlagajo izboljšave ali celo produkte sami izboljšujejo.

Pogovor s (potencialnim) uporabnikom je najboljša oblika intervjuja. V splošnem se predlaga več kot 10 (pri manj kot 10-ih intervjujih obstaja velika verjetnost, da se spregleda pomembna informacija) in manj kot 50 intervjujev (več kot 50 intervjujev le malo prispeva k kvantiteti in kvaliteti informacij).

Če sta uporabnika produktov le dve korporaciji, se predlaga intervjuje z večjim številom zaposlenih v isti korporaciji.

Pri interakciji z uporabnikom (ne glede na način pridobivanja podatkov) produkta se je potrebno izogniti konfliktom ter objektivno sprejemati informacijo brez zagovarjanja in opravičevanja slabših lastnosti našega obstoječega produkta ali vzpodbujanje kritike konkurenčnega produkta.

Pred intervjujem je potrebno vedeti, katere podatke moramo z intervjujem pridobiti. Za to moramo poznati cilje projekta, ciljni trg za produkt in ključne poslovne cilje. Navadno cilj projekta, ciljne trge za produkt in ključne poslovne cilje določi jedro projektnega team-a s konsenzom. Pred intervjujem je potrebno določiti tudi obliko intervjuja. Vprašanja naj bodo enostavna in generična, brez namigovanj na specifične ideje za nov produkt.

Intervjuje navadno izpelje marketing projektnega team-a. Pogosto pomagajo tudi ostali sodelavci iz trženja oziroma marketinga. Pri intervjuju so zaželeni:

- Spodbujanje drugačnega razmišljanja.
- Spodbujanje z alternativami, ko se učinkovitost intervjuja zmanjša.
- Izogibanje predpostavkam ali omejitvam, ki jih ima produkt, ki ga želimo zamenjati.
- Pripravljenost na presenečenja, ki so lahko priložnost za prave inovacije.

Da se ne izgublja pomembnih informacij se intervjuji snemajo (zvokovni in slikovni zapis), fotografirajo, zapisujejo,...

Pisna zahvala intervjujancem, je na mestu.

Poleg intervjujev se za identifikacijo potreb lahko uporabljajo tudi drugačni pristopi, kot je pasivno opazovanje kupca ali aktivna uporaba izdelka, uporabljajo se lahko različne delovne skupine in izkušeni testni odbori, ki pa so po mnenju večine manj učinkoviti kot neposreden intervju z uporabnikom.

### **Interpretacija izraženih potreb uporabnika**

Rezultat intervjujev je »potpourri« najrazličnejših odgovorov, ki so pogosto nepopolni. Veliko je tudi nepomembnih informacij, informacij, ki se podvajajo, ali absurdnih želja ali trditev uporabnika. Z intervjuji se navadno dobi med 50 in 300 trditev uporabnika. Trditve, izjave in izražene potrebe uporabnikov je potrebno interpretirati, jih zapisati in smiselno organizirati po skupinah. Nekatere je smiselno čim prej izločiti.

Potrebe uporabnika razdelimo po njihovi pomembnosti. Lahko jih razdelimo na primarne (nujne potrebe - zahteve uporabnika) in sekundarne potrebe (želje uporabnika in še druge koristne lastnosti produkta).

Nov produkt mora zadovoljiti vse nujne potrebe. Želimo si, da bi produkt lahko zadovoljil čim več želja uporabnika, še zlasti, če teh ne zadovoljuje konkurenčni produkt. Druge potencialno koristne lastnosti produkta moramo prepoznati in poznati, vendar načrtovanje novega produkta ne bo temeljilo na njih.

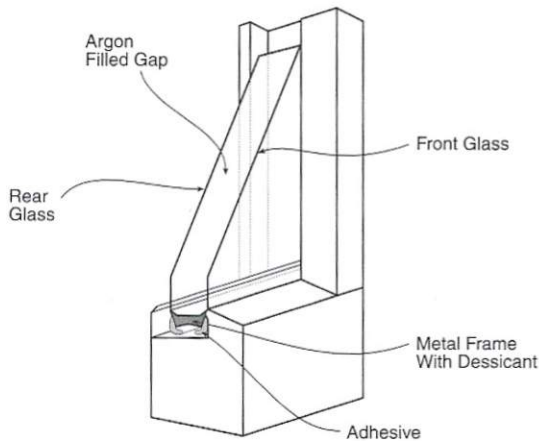
Način organiziranja in razvrščanja potreb po relevantnosti pri razvijanju novega produkta se razlikuje od organiziranja in razvrščanja pri izboljšavah obstoječega produkta. Ko izboljšujemo obstoječi produkt, je hierarhična razvrstitev potreb po pomembnosti bolj enostavna. Ko pa načrtujemo popolnoma nov produkt, je pogosto potrebna še dodatna pomoč uporabnikov (še intervjuji drugih uporabnikov ali pa ponovni intervjuji) pri podrobnejši analizi potreb ter njihovem razvrščanju.

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

### EXAMPLE 2.1–1 BETTER THERMOPANE WINDOWS

In hot or cold climates, windows must provide insulation as well as allow the entrance of light. To provide this insulation, windows often consist of two or more panes of glass, narrowly separated by a gap, as shown in Figure 2.1–1. Ideally, this gap would be evacuated, but the vacuum can pull the panes of glass together.

As a result, the gap between the windows is filled with a gas and glued with a sealant. The gas should have a low thermal conductivity to be an effective insulator. Because thermal conductivity in a gas is proportional to the inverse square root of the molecular weight, the best gas would have the highest molecular weight. Historically, freons such as  $\text{CCl}_2\text{F}_2$  (mol. wt. 121) were used. Since freons have



**Figure 2.1–1. A Thermopane Window.** The space between the panes is now filled with argon, a replacement for freon. The argon can leak out and water vapor can leak in; each can cause problems.

been phased out, argon (mol. wt. 40) is the industry's choice, even though its thermal conductivity won't be that much different from that of air.

However, the problem with the windows is less the insulation that they provide than their appearance. This appearance relies on the sealant used to glue the glass panes together. Water vapor diffuses through this sealant into the gas gap between the window's panes. This water vapor can then condense when the weather cools, fogging the window. To avoid this, manufacturers put a dessicant between the window panes, but this becomes saturated with time. In addition, the argon can leak out faster than air leaks in, causing the panes to bend together. Invent a better window sealant.

#### SOLUTION

This example is unusually straightforward. The most important customers for this sealant are the manufacturers of thermopane windows, whom you definitely will want to interview. You may also want to talk to some building contractors to discover if window fogging depends on how the window is installed or where in the house it is located. You probably will gain less from talking with homeowners, even though they are the eventual buyers of the windows.

The key questions you want to ask are also straightforward:

1. What are the requirements of the sealant?
2. What sealants have already been tried?
3. What is the temperature change that the window encounters?
4. What is the window lifetime?

Although there are many other questions which are helpful, they are not as central.

The answers to these questions are unambiguous. The sealant has two main functions: sealing the window panes together, and keeping argon in and water vapor out. The first of these requirements is essential; the second is that which can compromise current thermopane windows. While over 100 sealants have been carefully tried, silicone rubber gives by far the best seal. However, it is highly permeable to water vapor: the permeability of water is around  $4 \times 10^{-4}$  cm<sup>2</sup>/sec, about forty times faster than diffusion coefficients in normal liquids. One commonly used alternative to silicone rubber is polyisobutylene, because its permeability to water is about 400 times less than silicone rubber. However, polyisobutylene does not make as good a seal: it does not stick to the glass walls.

Questions 3 and 4 are important to window manufacturers, but have less impact on the choice of a sealant. Most windows encounter diurnal temperature changes of less than 15°C. Despite this, in an effort to test their products under higher stress, window manufacturers can use swings of three or more times this. Window lifetimes are normally expected to be more than twenty years. However, because few people own their homes this long, the key may be to avoid water condensation for only as long as the average homeowner stays in that particular house.

The need is thus for a sealant that bonds as well as silicone rubber, but that has a water permeability at least as small as polyisobutylene.

#### **EXAMPLE 2.1-2 ALTERNATIVE FLUIDS FOR DEICING AIRPLANES**

Minneapolis–St. Paul has a major airport with over 400 flights daily. This high traffic reflects the use of the airport as a hub by a major airline. This city is infamous for its cold winters. In the winter, snow can collect on planes as they wait at the gate for take-off. As shown in Figure 2.1-2, the snow is removed by spraying the planes with deicing fluids, which are discarded after use. These fluids are often discharged directly into groundwater, even though they can be toxic to humans and wildlife. In major airports like Minneapolis–St. Paul, the discharged deicing fluid is sewered, causing a major burden on the local sewage treatment plant. These deicing fluids cause major pollution.

Find alternative deicing fluids that are environmentally less abusive because they are easily recycled.



**Figure 2.1-2. Deicing Aircraft.** Snow is removed by spraying the planes with a 70°C aqueous solution of 50 wt. % ethylene glycol. We seek an alternative deicer that can be recycled.

## SOLUTION

In this case, we already have a product that works well, and we seek alternatives that not only work well but cause less pollution. Interestingly, our customers are not the airlines but the airports. In practice, the airports contract deicing to local engineering firms. We should interview the engineering firms' employees who are directly responsible for the deicing.

A synopsis of these interviews is given in Table 2.1-1, following the format suggested above. The synopsis does not contain some important information that does not easily fit into this format. First, all airports and all airlines are worried about this pollution problem. Some airlines are considering a special hanger with infrared heaters, an interesting idea for airplanes fully loaded with fuel! While North American airlines insist on virgin ethylene glycol, Dutch airports distill the effluent and recycle the glycol.

**TABLE 2.1-1 Interview Results for Deicing Fluids**

**What do you do now?**

"We no longer deice at the gate, because this was too difficult to control. Instead, when they are ready for take-off, aircraft are moved to a central location for deicing. We collect the run-off from the deicing in underground tanks and then slowly bleed it off to the sewage treatment plant."

**How do you use the product?**

"We spray with a 70°C solution of 50% water and 50% ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH). We spray for 10 minutes or till there is no snow visible, whichever is longer. We then spray with anti-icing fluids." (These are snow-melting hydrogels that adhere to the aircraft while it is waiting to take off, but are removed by shear during take-off. In this example, we ignore anti-icing fluids.)

**What features of the product work?**

"It's a good product. It works even at -30°C. It isn't volatile. It doesn't cause corrosion, like salt. It's hard to burn." (Once burning, it has a rate of combustion per kilogram around one third that of ethane.)

**What features of the product don't work?**

"None. It has some odor, and some passengers get sick, but not many. The effluent contains about 2% ethylene glycol, which is toxic to fish. The environmental agencies say it is probably toxic to humans, but I'm not convinced it is. Still, they won't let us discharge it, and they're always threatening to shut us down."

**How do you buy the product?**

"We get it through the State of Minnesota, who require bids. One company has the largest share but we always have at least two suppliers to ensure some competition."

*Note:* This is a synopsis of conversations with engineers responsible for deicing aircraft.

We next want to extract from the interviews the key characteristics that a perfect product would have. In this case, we conclude that the perfect product

1. is sprayable;
2. has a low volatility;
3. does not smell;
4. is not toxic to fish;
5. is not toxic to humans; and
6. is easily recycled.

These characteristics imply no surprises.

However, Table 2.1–1 also shows that the interviews contain contradictions and redundancies. We want to remove these in our list of characteristics of a perfect product. For example, the product cannot be nonvolatile and still smell. The smell makes some passengers sick, so the product is volatile. As a second example, the product should be nontoxic to fish, humans, and everything else. We do not need to list these characteristics separately.

The key product attributes chosen in this case, given in Table 2.1–2, merit a brief discussion. That the product should melt snow is obvious, but a good reminder that we must soon choose a useful temperature range ( $-30^{\circ}\text{C}$  to duplicate the glycol). Applying the product must be easy; spraying is one obvious alternative. The idea that the product cannot be highly toxic is self-evident, so we have chosen the more specific term “noncarcinogenic.” Clearly, the product should not easily burn, but we have not made this essential because we feel that, with good practice, we can mitigate this risk. With this table, we are poised to seek ideas for this new, recyclable deicer.

**TABLE 2.1–2 Characteristics of Deicing Fluids**

<b>Essential</b>	<b>Desirable</b>	<b>Useful</b>
The product must melt snow.	The product is noncarcinogenic.	The product is inexpensive.
It must be easily applied.	It is nonflammable.	It is water miscible.
It must be noncorrosive.	It is easily recycled.	It is available from multiple suppliers.

*Note:* This table organizes the more scattered topics in Table 2.1–1.

### **EXAMPLE 2.1–3 “SMART” LABELS**

Your company currently manufactures the labels to attach to food in supermarkets. For example, the labels attached to packaged chicken could give the weight, the price per kilogram, the price of the package, and the date by which the chicken should be eaten. Although your labels are a successful product, you want to improve them so they tell the consumer more about the chicken. For example, the date on such a “smart” label might change if the chicken were frozen.

Your core team has decided that your goal is to make labels that let consumers judge product quality. The team has also decided to focus on the food and pharmaceutical areas, building on company experience with its current labels.

Identify and organize customer needs for these new smart labels.

### **SOLUTION**

To investigate this new product, we cannot easily use our standard questions, suggested above, because we are not improving an existing product, but developing a new one. We do not have good general guidelines. Instead, we begin by assembling several peers and collecting their thoughts. Then we organize these ideas, at least in a preliminary fashion.

Our efforts to identify needs are partially summarized in Table 2.1–3. Although this list is abridged, it is not edited. In this abridgement, we did not exclude obvious tangents or irrelevancies. For example, idea 13 implies that the chemistry used for smart labels could be used for better condoms. Now it is true that there could be a

major market for condoms that gave their users greater pleasure by, for example, releasing sexual stimulants. Such condoms might be more widely used, and hence reduce the spread of the HIV virus. But your current company is very unlikely to jump from food labeling into condom manufacture. This irrelevant idea has value only in waking up any who are dozing.

**TABLE 2.1-3 Customer Needs for “Smart” Labels**

1. We need labels to tell if the chicken has spoiled.
2. Similar labels would be useful for ground beef.
3. Smart labels should say if ice cream has ever melted.
4. They should say if the chicken ever got warm.
5. The best labels would be stamped onto meat, like the current USDA inspection stamps.
6. Labels on canned goods would be good, too.
7. Canned goods labels should detect botulism.
8. Stick-on labels are better.
9. Labels should remind you when drugs go bad.
10. Some labels could release drugs slowly.
11. Nicotine patches are one good smart label.
12. Could labels also release good smells?
13. This technology could be used to make better condoms.
14. Dairy goods should have some way to show their temperature history.
15. These labels could respond to lactic acid, so you could tell if the milk had spoiled.
16. You tell if things are spoiled by smelling them.
17. Labels for cream should tell you just before the cream turns sour.
18. Labels for milk should too.
19. Eggs do not spoil much.
20. Labels for frozen foods could say if they have ever been thawed.
21. Beer labels should say if it is at the right drinking temperature.
22. Wine labels could, too.
23. Labels for fish should indicate that it has no smell.
24. We need labels for mussels.
25. How can color-blind people use labels that change color?
26. Eggs should be thrown away when their stated shelf life expires.
27. Pharmaceuticals stay useful long past their stated dates.
28. Prescription drugs are usually finished, so there is no need for smart labels.
29. Could the labels be activated by the customer?
30. These would be like Post It notes that tell you when you must eat specific foods.
31. These must be activated by the consumer.
32. They could be part of tamper-proof packaging, activated automatically by opening the package.
33. Some labels could be irreversible: once they change, they should not change back.
34. The most important question is “Has this food ever been warm?”
35. These labels are especially important for caterers.
36. Labels could respond to pH changes as well as temperature changes.

Once we have a collection of needs such as those in Table 2.1-3, we must organize them. In cases as unstructured as this one, it is probably best to organize them not around business topics but around intellectual topics, as shown in Table 2.1-4. From this outline, we can target product needs consistent with our company’s business interests. We could choose to develop labels that use thermally triggered, irreversible reactions as our initial focus. We could choose labels that detect spoilage or are consumer activated as secondary needs. However, choosing product needs for final development will clearly require taking these organized needs back to our customers for further definition.



**TABLE 2.1-4 One Possible Organization of "Smart" Label Needs**

- I. Temperature
  - A. Actual temperature assessed  
Beer and other foods (21, 22)
  - B. Temperature history assessed (14, 34)  
Implies irreversible reactions (33)
  - C. Target: foods (3, 4, 20)
- II. Spoilage
  - A. Anticipate spoilage (17, 18, 30)
  - B. Detect spoilage (15, 16)
  - C. Targets: foods (1, 2, 23, 24) and drugs (9, 27, 28)
- III. Customer activated labels (29, 31)
- IV. Tangents
  - A. Label materials (5-8)
  - B. Controlled release (10-12)

*Note:* This table organizes the needs listed in Table 2.1-3. The numbers in parentheses refer to that table; needs 13, 19, 25, 26, and 35 are omitted.

This is a good example. As a reader, you can teach yourself much more about evaluating customer needs by repeating this example than by reading the text. At this stage of product design, you will almost certainly get results different from those given above. Indeed, when we have repeated our interviews, we also got somewhat different results. These differences disappear as we continue with the product design.

### 3.2 POTREBE POTROŠNIKOV PRI POTROŠNIH PRODUKTIH

Potrebe ali zahteve uporabnikov kemijskih produktov želimo kvantitativno izraziti (z meritvami s poznanimi tehnikami).

Velikokrat pa je merjenje pomembnih lastnosti potrošnih produktov s konvencionalnimi metodami nemogoče (npr. kako določiti gladkost kože po uporabi kreme ali kako določiti mehko volne ali hrustljivost piškota). Takrat je potrebe uporabnika (potrošnika) težko prevesti v specifikacije produkta.

#### Potrošnikova ocena produkta

Ko se ocenjuje potrošni produkt, je glavna težava izbira primerne načina ocenjevanja. Najpogosteje se uporabljajo primerjalni test, razvrščanje produktov po vrstnem redu oziroma uporaba ocenjevalne lestvice ter ocenjevanje z uporabo relativnih vrednosti.

- Primerjalni test: "Ali je vzorec A boljši kot vzorec B?"  
"Ali je sladoled A bolj kremozen kot sladoled B?"

Primerjalne ocene različnih potrošnikov se po testu povprečijo. Seveda je potrebno biti pozorni na ocenjevalčevo verodostojnost. Z oceno "A je boljši od B, C je boljši od A, B je boljši od C" je nekaj narobe.

- Razvrščanje vzorcev po kakovosti od najboljšega do najslabšega brez uporabe ocenjevalne lestvice:  
"C > D > A > B > E "

ali z uporabo ocenjevalne lestvice npr. od 1 (najslabše) do 10 (najboljše):

"A: 6, B: 5, C:10, D:8, E:2"

Ocenjevalna lestvica nam pove več. Pove nam koliko se produkti med seboj razlikujejo. Izračuna se povprečna ocena produkta - aritmetično povprečje ocen. Pomembno je, da ocenjevalec pri ocenjevanju uporablja celotno skalo (v tem primeru od 1 do 10). Vedeti moramo, kaj je povprečna ocena (v tem primeru 5.5 in ne 5!).

- Ocenjevanje vzorcev z uporabo relativnih vrednosti: Izberemo referenčni vzorec, kateremu pripišemo neko vrednost. Ostale vzorce primerjamo z referenčnim vzorcem po vrednosti.

"Piškot A je sladek  $n_0$ . Piškot B je dvakrat slajši in ima vrednost  $2n_0$ . Piškot C je za tretjino manj sladek kot piškot A in je sladek  $2/3n_0$ ..."

Računanje povprečij je v tem primeru bolj zapleteno, ker lahko vsak ocenjevalec izbere svoj referenčni vzorec. Zato najprej za vsakega ocenjevalca izračunamo povprečno vrednost njegovih ocen (geometrično povprečje). Nato izračunamo relativne vrednosti njegovih ocen tako, da prvotne vrednosti (ocena ocenjevalca) delimo s povprečno vrednostjo. Povprečna vrednost ocene produkta je geometrično povprečje relativnih vrednosti ocen vseh ocenjevalcev.

### **Potrošnikova ocena in instrumentalna analiza**

Potrošnikove kvalitativne ocene želimo kvantificirati iz več razlogov. Pri razvijanju novega produkta želimo biti hitri in učinkoviti. Želimo vedeti, koliko je nov produkt boljši od starega ali pa koliko smo izboljšali ali poslabšali produkt s spremembo njegove sestave. Zato v razvoju produktov uporabljamo instrumentalne ali druge analitske tehnike.

Navadno se zveza med potrošnikovo oceno neke lastnosti produkta in rezultatom instrumentalne analize poišče empirično. Pogosto je zveza predvidljiva. Na primer »gosta« juha ima višjo viskoznost kot »redka« juha. Viskoznost oziroma reološke lastnosti juhe določamo z reometrom. Višja kot je viskoznost juhe, bolj jo bo potrošnik označil za »gosto«. Enako je »sladkost« premosorazmerna s koncentracijo sladkorja, »kislost« pa s koncentracijo kisline.

Včasih pa je zveza med potrošnikovo oceno lastnosti produkta in rezultatom instrumentalne analize nepričakovana. Na primer pričakovali bi, da je »hrustljivost« žitnih kosmičev odvisna od njihove mehanike loma. Presenetljivo je občutek hrustljivosti povezan predvsem z zvokom, ki se nastaja pri žvečenju kosmičev. Podobno bi pričakovali, da je »gladkost« (»smoothness«) piva odvisna od njegove viskoznosti, pa ni. Odvisna je od velikosti mehurčkov v pivu – manjši so, bolj bo pivo »gladko«.

Ker pa potrošnikovih ocen določenih lastnosti produktov ni mogoče dovolj dobro povezati z rezultati dostopnih instrumentalnih metod, se razvijajo specifični instrumenti, ki bolje posnemajo potrošnikovo uporabo in oceno. Ena bolj bizarnih rešitev je namestitev zobne proteze na gibljivi del instrumenta za dinamično mehansko analizo (za merjenje mehkoobe hrane, recimo zrezka).

Občasno lahko vidimo kako sta potrošnikova ocena in instrumentalna analiza kvantitativno povezani. Na primer: Če držimo v roki kovinsko žlico in leseno žlico, ki smo ju pravkar vzeli iz istega kuhinjskega predala, zaznamo, da je kovinska žlica hladnejša, čeprav imata obe isto temperaturo, ki je enaka sobni. To pa zato, ker je temperatura, ki jo zaznavamo, temperatura naše kože in ne temperatura predmeta, ki ga držimo v roki. Če ocenimo, kako termična difuzivnost kovine vpliva na temperaturo naše kože, lahko napovemo za koliko stopinj zgleda kovinska žlica hladnejša od lesene.

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

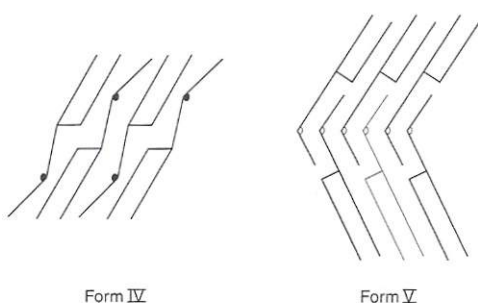
### EXAMPLE 2.2-1 TASTY CHOCOLATE

One of the attractive factors of good chocolate is its smooth “melt-in-the-mouth” quality. Some chocaholics even claim a pleasant cooling of the mouth, as the fat crystals in the chocolate absorb latent heat and melt. Sometimes chocolate exhibits a powder tan layer called “bloom,” especially when it is old and has been stored at fluctuating temperature. This chocolate has identical ingredients and chemical composition to tasty chocolate, but it has an unpleasant powdery texture in the mouth.

Chocolate manufacturers, such as Nestlé, employ expert panels in order to assess the quality of their chocolate. These testers are extremely competent – some can even identify the country of origin of the cocoa beans, in much the same way an expert oenologist can tell the chateau of a fine wine. The testers do a good job. However, it would be quicker, cheaper, and perhaps more reliable if we could augment some of their assessments by using scientific instruments.

### SOLUTION

Chocolate gets its melt-in-the-mouth sensation from the melting of cocoa butter crystals. Cocoa butter is a triglyceride, similar to olive oil, margarine, and animal



**Figure 2.2-1. Schematic Structures of Forms IV and V of Cocoa Butter.** Individual triglyceride molecules adopt “chair” structures. In Form IV, these chairs stack with a repeat distance approximately two times the length of a single fatty acid chain. In Form V, this repeat distance is about three times that in Form IV. Form V tastes better.

fat. Although triglycerides are the commonest form of naturally occurring fat, most have a poorly defined melting point because they contain a range of different fatty acids. Cocoa butter is unusual in having a narrow range of composition; it mainly consists of symmetrical triglycerides with oleic acid (unsaturated) in the 2- position and palmitic or stearic acid (saturated) in the 1- and 3- positions. This results in a well-defined crystal structure and a sharp melting point. However, cocoa butter can crystallize into five different crystal forms, each with its own melting point. Which one is formed depends on the exact preparation recipe. This is why confectionery chefs worry so much about cooling rate and stirring speed when preparing chocolate dishes from the melt. Form V is the desirable one, with a melting point of about 35°C, just below mouth temperature. Form IV, produced by cooling rapidly without stirring, has a melting point of about 28°C and is believed to be the cause of bloom. The structures of forms IV and V are shown schematically in Figure 2.2-1.

In effect, chocolate testers spend a lot of effort in identifying crystal forms of cocoa butter. We can do this more reliably and quicker with the use of differential scanning calorimetry (DSC). In this method we measure the rate of heat flow as the temperature is raised: as the crystals melt, energy is absorbed in the form of latent heat, without a concomitant temperature increase. We identify the presence of different crystal forms by the presence of different melting points in DSC. If

we wish to be more quantitative, we can use the more sophisticated and expensive technique of powder X-ray diffraction, which shows how much of each crystal form is present. We can then assess product quality and so optimize manufacturing and storage procedures.

**EXAMPLE 2.2–2 THE CONSUMER ATTRIBUTE “VISCOSITY”**

Studies of skin creams show that the consumer attributes of “thick” and “viscous” are closely related and that both are correlated with instrumental measurements of viscosity. However, the correlation is not linear:

$$\begin{aligned} (\text{assessments of “thick”}) &\propto (\text{assessments of “viscous”}) \\ &\propto \sqrt{\text{measurements of viscosity}}. \end{aligned}$$

Suggest why this could occur.

**SOLUTION**

The obvious hypothesis is that “viscous” skin creams cause larger forces when rubbed on the skin. The force  $F$  is related to the viscosity  $\mu$  by

$$(\text{assessments of “viscous”}) \propto F = -\mu A \frac{dv}{dy},$$

where  $A$  is the area of the fingers,  $v$  is the fluid velocity, and  $y$  is the distance normal to the finger surface. The area is constant; because the layer of skin cream is thin, the derivative equals the finger speed  $v$  divided by the cream thickness  $h$ . Thus

$$(\text{assessments of “viscous”}) \propto \frac{\mu v}{h}.$$

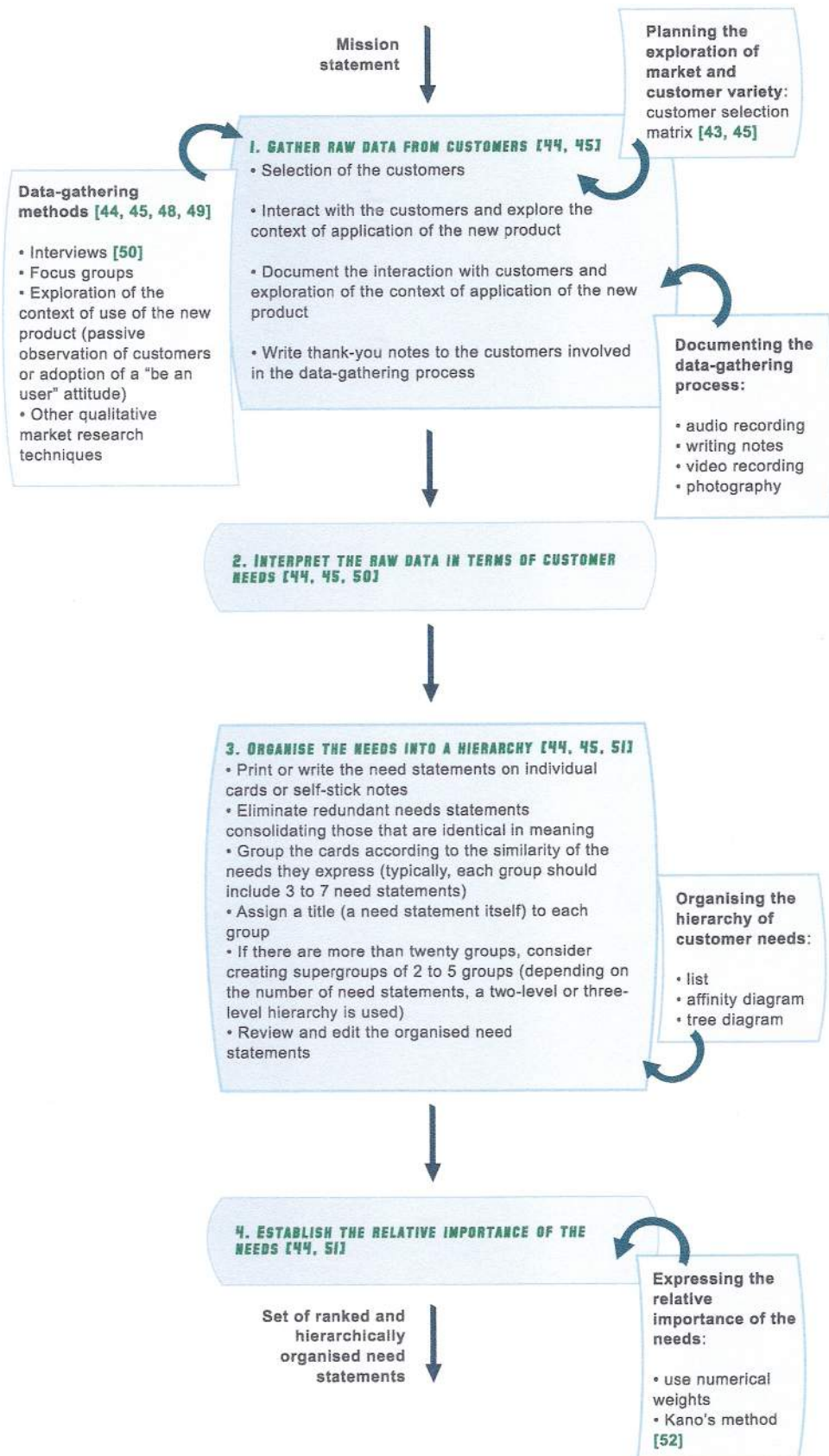
However, more viscous creams will have a thicker layer  $h$  on the surface. In fact, from a calculation by Clerk Maxwell, we may show that  $h$  is proportional to  $\mu^{1/2}$ . Thus, because the finger velocity  $v$  is observed to be constant,

$$(\text{assessments of “viscous”}) \propto \frac{\mu v}{\mu^{1/2}} \propto \mu^{1/2}.$$

Similar arguments for power-law fluids are consistent with experiments, lending further support to this hypothesis.

Shematski prikaz identifikacije potreb:

Vir: [http://www.engsc.ac.uk/an/mini\\_projects/cpd/index.html](http://www.engsc.ac.uk/an/mini_projects/cpd/index.html) (6.9.2011)



Systematic approach to customer needs identification.

Primer identifikacije idej: Nov premaz.

Vir: [http://www.engsc.ac.uk/an/mini\\_projects/cpd/index.html](http://www.engsc.ac.uk/an/mini_projects/cpd/index.html) (6.9.2011)

### 3.3 PREVEDBA POTREB V SPECIFIKACIJE PRODUKTA

Potrebe uporabnikov so v intervjujih v veliki meri izražene kvalitativno, vključujejo predloge za trivialne spremembe obstoječega produkta in tudi nerealne želje. Zbiranje in urejanje potreb je predvsem domena marketinga. Jedro projektnega team-a, katerega osnovna znanja so znanja kemije in inženirstva, pri tem nudi strokovno oporo in predvsem dobro kritiko.

Pri prevedbi potreb uporabnikov v specifikacije produkta pa so gonilna sila predvsem kemiki in inženirji. Marketing igra tu manj pomembno vlogo.

Ko na osnovi identificiranih potreb definiramo specifikacije produkta, je največkrat primerno naslednje zaporedje aktivnosti:

1. Zapis kemijskih reakcij za vse kemijske procese, ki potekajo pri uporabi produkta.
2. Zapis snovnih in energetskih bilanc pri uporabi produkta.
3. Ocena hitrosti vseh procesov pri uporabi produkta.

Zapis kemijskih reakcij je za ljudi s kemijsko izobrazbo trivialen. V tem koraku se ne sme pozabiti, da v kemijski reakciji med seboj reagirajo moli snovi v določenem stehiometričnem razmerju.

Zapis snovnih, navadno masnih, bilanc in energetskih bilanc je osnovan na termodinamskih zakonitostih in nam pove kaj se v sistemu lahko zgodi. Na primer: maksimalna sprememba volumna, končna temperatura po reakciji pri adiabatnih pogojih, velikost reciklov... Pri zapisu bilanc v tej fazi načrtovanja produkta iščemo najbolj enostavno rešitev, ki ni trivialna. Predpostavljamo, da se snovne lastnosti ne spreminjajo s temperaturo ter da so raztopine idealne. Ta korak je trivialen za ljudi s kemijsko inženirsko izobrazbo.

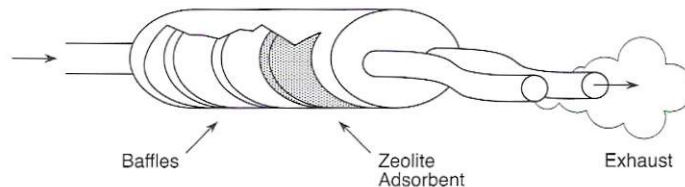
Tudi pri oceni hitrosti kemijskih in fizikalnih procesov (v tej fazi načrtovanja produkta) uporabljamo številne poenostavitve. Predpostavimo, da so transportni koeficienti (termična prevodnost, difuzijski koeficienti) konstantni. Če s tem ne naredimo večje napake, predpostavimo, da so tekočine Newtonske. Podobno, predpostavljamo, da so kemijske reakcije prvega ali ničtega reda, da je hitrost kemijske reakcije difuzijsko ali kinetično kontrolirana. Tudi ta korak mora biti trivialen za ljudi s kemijsko inženirsko izobrazbo.

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

### EXAMPLE 2.3–1 MUFFLER DESIGN

Automobile mufflers (in Britain, “silencers”) rust from the inside out. They do this because after the car is driven, the muffler contains exhaust gases, including water vapor. When the muffler cools, the water condenses and corrodes the inside of the muffler.

One clever route to avoid this problem is to put a small bag containing hydrophilic zeolite in the muffler, as shown in Figure 2.3–1. This adsorbs the water vapor, preventing liquid condensation and so dramatically reducing corrosion.



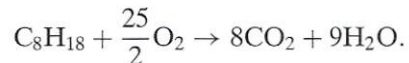
**Figure 2.3–1. Car Mufflers with Reduced Corrosion.** The proposed muffler would contain a small amount of zeolite, which absorbs water left in the muffler when the car’s engine is shut off. The water is released when the car is restarted and the muffler again gets hot.

When the car is restarted, the hot exhaust gases heat the zeolite and drive off the adsorbed water. The zeolite is then ready to adsorb more water when the engine is stopped.

We are considering making a muffler that has this feature. How much water will we need to adsorb? How fast should the adsorption be?

#### SOLUTION

This problem is simply an exercise in stoichiometry. Assume the muffler’s volume is about 5 L, and that is it about 70% voids. The basic reaction in the engine is



If the engine is run with 10% excess air, then the exhaust concentration at complete combustion is easily shown to be 0%  $\text{C}_8\text{H}_{18}$ , 2%  $\text{O}_2$ , 75%  $\text{N}_2$ , 11%  $\text{CO}_2$ , and 12%  $\text{H}_2\text{O}$ . Thus

$$\left(\frac{5\text{ L}}{22.4\text{ L/gmol}}\right)0.7\left(\frac{0.2\text{ gmol H}_2\text{O}}{\text{gmol total}}\right)\frac{18\text{ g}}{\text{gmol}} = 0.34\text{ g H}_2\text{O}.$$

Adsorbing this small amount can prolong the life of the muffler. We want the adsorption to be prompt, but it need not be faster than the time that the muffler takes to cool. Thirty seconds is probably a reasonable starting point.

### **EXAMPLE 2.3–2 WATER PURIFICATION FOR THE TRAVELER**

People traveling into wilderness areas require drinking water. Often water sources such as streams and ponds are contaminated by viruses and bacteria. A particular problem in North America is giardia, a protozoan present in 90% of water sources. (It is carried by animals as well as humans, which explains its wide spread.) Giardia results in severe intestinal problems, with very unpleasant symptoms including noxious farts with a sulfurous tang, which is particularly unfortunate if you are sharing a tent.

Interviews with customers (hikers, mountaineers, soldiers, and equipment suppliers) might reveal the following list of needs in a water purification device:

- Produces safe water
- Is light and small
- Is fast acting
- Has a long lifetime
- Requires no power source
- Is cheap and reusable
- Improves odor and flavor

Write specifications for a water purification product.

### **SOLUTION**

This problem is somewhat different from that just discussed because we are now considering a consumer product. For such products, the two steps of chemical reactions and thermodynamics suggested above are not helpful. The chemical reactions and mass and energy balances are trivial. There is a rate process at work: how fast do people lose water? The answer is about 5 L or 1 gal/day. Indeed, the original definition of a gallon derived from the daily allowance of water a farmer had to provide to each laborer.

This starts off our quantification, which in this case will be led more by intuition than science. We might aim to design for groups of two to four persons, for trips of up to 2 months. If each person needs around 5 L of drinking water per day, we need to be able to purify 2000 L of water before our product fails. We need around 20 L per day, but probably we would like to produce it all quickly, for example for cooking, so we want a flow rate of say  $1 \text{ L min}^{-1}$ . Because the product must be carried up mountains, it must weight less than 1 kg and occupy less than 1 L volume.

For safety we can look to legislation: U.S. health regulations require 99.9% removal of bacteria and protozoa in surface water treatment. Note we have focused here on bacteria and protozoa. This is appropriate in the North American wilderness, but if we were considering travelers in third world countries, we also need to worry about waterborne viruses, passed on through human waste. Here we have an example of different specifications for different markets. Price? Climbers will pay in excess of \$100 for a good ice axe, so one might expect they would be willing to fork out this much for clean water. The product must be effective over a full range of temperatures at which water is found and at altitudes up to 7000 m:  $0\text{--}40^\circ\text{C}$  and one third of 1 atm pressure.



Our final specifications might take the following form:

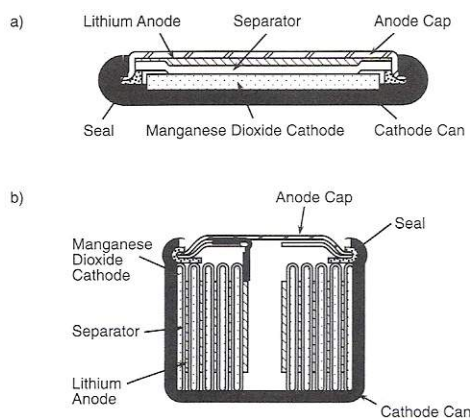
- Has a capacity of 2000 L
- Has a production rate of  $1 \text{ L min}^{-1}$
- Removes 99.9% of bacteria and protozoa
- Costs less than \$100
- Has an operating range of  $0\text{--}40^\circ\text{C}$ , one third of 1 atm
- Improves odor and flavor

We are now in a good position to start thinking of ways to achieve these specifications.

### EXAMPLE 2.3-3 PREVENTING EXPLOSIONS IN HIGH-PERFORMANCE BATTERIES

Modern electronic devices such as cellular phones and laptop computers require powerful batteries in order to function without frequent recharging. The result, shown schematically in Figure 2.3-2, is batteries with ever increasing power per volume and power per mass. Putting more and more energy into smaller and smaller packages means that the batteries are becoming bombs. Indeed, the president of one battery manufacturer had his car phone blow up in his ear while he was talking to his wife.

Obviously, there is a need for safe batteries that shut down before they blow up. How fast does the battery need to shut down?

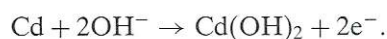


**Figure 2.3-2. High-Performance Batteries for Laptop Computers.** The high energy density of these batteries, especially those for laptop computers, means that accidental short circuits can cause explosions. The coin cell in a) is drawn on a larger scale than the cylindrical cell in b).

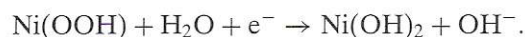
### SOLUTION

In answering this question, we consider the most powerful batteries available, which are based on lithium. Because chemical details of lithium batteries are hard to come by, we choose alkaline nickel-cadmium (NiCad) batteries as our standard. We can then extrapolate our results to lithium batteries, which are about five times more powerful. We also choose a laptop computer like the IBM Thinkpad as a standard application. This computer currently uses a battery with about 50 Whr energy.

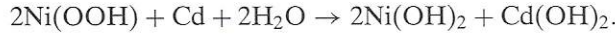
We begin by writing out the basic reactions during discharge. At the anode:



At the cathode:



The overall reaction is thus



This reaction is reversed during charging. The electrodes are separated by aqueous KOH, with a density of around  $1.2 \text{ g/cm}^3$ . This roughly corresponds to a concentration of 4 M. Under normal operations, the hydroxide concentration is nearly constant between the electrodes.

We now turn to the mass and energy balances. A battery in a laptop typically contains two electrodes around 3 mm thick, separated by a membrane separator. The membrane separator, which is around  $30 \mu\text{m}$  thick, contains about 30% pores filled with the 4 M KOH. The battery is usually about 20 cm square, so its total volume is around  $240 \text{ cm}^3$ .

The adiabatic temperature rise if the battery is shorted out is found from the first law of thermodynamics:

$$\Delta U = Q + W,$$

where  $\Delta U$  is the internal energy change,  $Q$  is the heat, and  $W$  is the work. Because the battery is adiabatic,  $Q$  is zero. Because the battery has a constant volume,  $W$  is zero. Because the battery contains no gas,  $\Delta U$  is about equal to the enthalpy change  $\Delta H$ . Thus

$$\Delta U = 0 = \Delta H_{rxn} + V\rho\hat{C}_p\Delta T,$$

where  $\Delta H_{rxn}$  is the heat of reaction under the initial conditions,  $V$  is the battery volume,  $\rho$  is its average density,  $\hat{C}_p$  is its average specific heat capacity, and  $\Delta T$  is the temperature rise caused by the short. Consistent with our goal of keeping our analysis simple, we assume that the battery is initially at  $25^\circ\text{C}$ , the normal reference temperature for chemical reactions.

The heat of reaction is the energy in the battery or ( $-50 \text{ Whr}$ ). An average value of  $\rho\hat{C}_p$  is about  $3 \text{ J/cm}^3 \text{ }^\circ\text{C}$ . Thus

$$0 = -50 \frac{\text{J hr}}{\text{sec}} \left( \frac{3600 \text{ sec}}{\text{hr}} \right) + 240 \text{ cm}^3 \left( \frac{3 \text{ J}}{\text{cm}^3 \text{ }^\circ\text{C}} \right) (\Delta T)$$

and

$$\Delta T = 250^\circ\text{C}.$$

At this temperature, the water will have turned to steam and the battery will explode. We may be in trouble. This completes our summary of the mass and energy balances.

Next, we turn to calculating the rate at which the battery heats up when it is shorted out. When the battery is shorted, the electrochemical reactions shown above are controlled by the rate of hydroxide diffusion from one electrode to the other. Thus the time taken to discharge a shorted battery is roughly given by

$$\begin{aligned} (\text{amount Cd in battery}) \left( \frac{2 \text{ mol OH}^-}{\text{mol Cd}} \right) &= \left( \frac{\text{OH}^- \text{ flux}}{\text{area time}} \right) (\text{area}) \text{time} = j_1 A t \\ &= \left( \frac{D}{\delta} \Delta c \right) A t, \end{aligned}$$

where  $j_1$  is the hydroxide flux,  $D$  is its diffusion coefficient,  $\delta$  is the thickness between the electrodes,  $\Delta c$  is the hydroxide concentration difference, and  $A$  is the battery area. NiCad batteries normally have about  $100 \text{ C Cd/cm}^3$  in the anode, which occupies roughly half the battery volume; the diffusion coefficient of the hydroxide is about  $5 \times 10^{-5} \text{ cm}^2/\text{sec}$ . Thus

$$\frac{100 \text{ C Cd}}{\text{cm}^3} \left( \frac{1/2(240 \text{ cm}^3)}{96500 \text{ C/mol}} \right) \left( \frac{2 \text{ mol OH}^-}{\text{mol Cd}} \right)$$

$$= \left( \frac{5 \times 10^{-5} \text{ cm}^2/\text{sec}}{30 \times 10^{-4} \text{ cm}} \frac{4 \text{ mol OH}^-}{10^3 \text{ cm}^3} \right) 400 \text{ cm}^2 \text{ t};$$

$$t = 10 \text{ sec.}$$

However, we must shut down the battery before any vaporization. Because we start at 25°C, we can only stand a temperature change of 75°C. Thus

$$t = \frac{75}{250}(10) = 3 \text{ sec.}$$

The customer's need is not to be blown up. The resulting product specification is to shut down the battery within about 3 sec.

### 3.4 PREVERJANJE SPECIFIKACIJ PRODUKTA

Uporaba stehiometrije, snovnih in energetskih bilanc ter zapisa hitrosti procesov privede do prvih preeliminarnih specifikacij produkta. Navadno lahko preeliminarne specifikacije produkta kar dobro ocenimo. Na žalost, pa se dogaja tudi, da so preeliminarne specifikacije nesprejemljive. Zato je pogosto potrebno preverjanje oziroma revizija specifikacij produkta.

Preeliminarne specifikacije so lahko nesprejemljive, ker so popolnoma nerealistične. Na primer materiali so bistveno predragi, koncentracije, tokovi, tlak so previsoki, elementa ni v periodnem sistemu...

Različne gospodarske družbe imenujejo ta korak različno. Na primer: "sanity check", "gut check", "back of the envelope calculation", "chicken test"...

Revizija specifikacij produkta je potrebna tudi zato, da preverimo ali bo nov produkt sploh imel prednosti pred obstoječim produktom ali konkurenčnim produktom. Obstaja možnost, da so preeliminarne specifikacije novega produkta slabše od specifikacij referenčnega produkta (obstoječega ali konkurenčnega produkta). Zato se v tem koraku naredi primerjava specifikacij novega in referenčnega produkta ("benchmark"). Če referenčni produkt ne obstaja, lahko za primerjavo izberemo tudi produkt z isto uporabno funkcijo, katerega delovanje temelji na drugačni kemijski osnovi.

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

### EXAMPLE 2.4-1 DEICING WINTER ROADS

In winter, roads in areas of frequent frost are spread with a mixture of sand and salt to improve traction and melt ice and snow. Although this treatment works well to about  $-20^{\circ}\text{C}$ , the salt causes significant environmental damage. It corrodes cars about four times faster than water alone. It weakens bridge decks and parking ramps, sometimes causing their collapse. It can pollute local water wells.

Not surprisingly, government agencies frequently look for alternative chemicals to salt that are environmentally less abusive. Using salt as a benchmark, they suggest the following specifications for the alternative chemical:

1. It should melt ice over a similar temperature range.
2. It should melt a comparable amount of ice per kilogram as salt does.
3. It should cause less corrosion per kilogram than salt.

Two alternatives to salt that are frequently suggested are urea and calcium magnesium acetate, often called "CMA."

Compare the performance of salt with these alternatives as a means of revising product specifications.

### SOLUTION

To make this comparison, we must first consider why chemicals cause ice to melt. The basic phenomenon is freezing point depression. When any solute is dissolved in water, the chemical potential of the water molecules is lowered. As the temperature is lowered, this chemical potential also drops, but not as fast as that of ice does. When the chemical potential of the water in solution becomes higher than that of ice, the water freezes.

To put these ideas on a more quantitative basis, we remember that at the freezing temperature  $T$ , the chemical potential  $\mu_1$  of the water in the ice equals that in a solution of water of mole fraction  $x_1$ ,

$$\mu_1(\text{ice}, T) = \mu_1(\text{pure liquid water}, T) + RT \ln x_1.$$

This implies an ideal solution, consistent with our strategy of choosing the simplest nontrivial case. Because the solution is dilute,  $x_1$  is close to unity and

$$\ln x_1 = \ln(1 - x_2) \doteq -x_2 - \dots,$$

where  $x_2$  is the mole fraction of the chemical. Combining these expressions gives

$$x_2 = \frac{\mu_1(\text{pure liquid water}, T) - \mu_1(\text{ice}, T)}{RT}.$$

We must now calculate the chemical potential difference.

The calculation of this chemical potential difference is easily reviewed, but those who want to avoid the review can skip this paragraph. By definition,

$$\frac{\mu_1}{RT} = \frac{\bar{H}_1 - T\bar{S}_1}{RT} = \frac{\bar{H}_1}{RT} - \frac{\bar{S}_1}{R}.$$

In the case of a pure substance,

$$\mu_1 = \underline{G}_1, \quad \bar{H}_1 = \underline{H}_1, \quad \bar{S}_1 = \underline{S}_1,$$

where  $\bar{H}_1$  and  $\bar{S}_1$  are the partial molar enthalpy and entropy, respectively; and  $\underline{G}_1$ ,  $\underline{H}_1$ , and  $\underline{S}_1$  are the molar Gibbs energy, enthalpy, and entropy of pure 1. As a result,

$$\begin{aligned} & \frac{\mu_1(\text{pure liquid water}, T) - \mu_1(\text{ice}, T)}{RT} \\ &= \frac{\underline{H}_1(\text{pure liquid water}, T) - \underline{H}_1(\text{ice}, T)}{RT} \\ & \quad - \frac{\underline{S}_1(\text{pure liquid water}, T) - \underline{S}_1(\text{ice}, T)}{R}. \end{aligned}$$

At the normal freezing point  $T_0$ ,

$$\begin{aligned} & \frac{\mu_1^0(\text{pure liquid water}, T_0) - \mu_1^0(\text{ice}, T_0)}{RT_0} = 0, \\ &= \frac{\underline{H}_1(\text{pure liquid water}, T_0) - \underline{H}_1(\text{ice}, T_0)}{RT_0} \\ & \quad - \frac{\underline{S}_1(\text{pure liquid water}, T_0) - \underline{S}_1(\text{ice}, T_0)}{R}. \end{aligned}$$

Subtracting these equations, and assuming the enthalpy and entropy of fusion to be temperature independent, we find

$$\begin{aligned} & \frac{\mu_1(\text{pure liquid water}, T) - \mu_1(\text{ice}, T)}{RT} \\ &= \{ \underline{H}_1(\text{pure liquid water}, T) - \underline{H}_1(\text{ice}, T) \} \left( \frac{1}{RT} - \frac{1}{RT_0} \right) \\ &= \{ \Delta \underline{H}_{\text{fusion}} \} \left( \frac{1}{RT} - \frac{1}{RT_0} \right) \\ &\doteq \left\{ \frac{\Delta \underline{H}_{\text{fusion}}}{RT^2} \right\} (T_0 - T) \end{aligned}$$

In this last equality, we have recognized that the freezing point depression is much smaller than the absolute temperature.

We now combine this free energy difference with our previous result to find

$$x_2 = \frac{\Delta \underline{H}_{\text{fusion}}}{RT^2} (T_0 - T).$$

This result, which may also be derived from the Gibbs-Helmholtz equation, shows how the solution concentration is related to the freezing point depression. For example, for a drop of  $10^\circ\text{K}$ ,

$$\begin{aligned} x_2 &= \frac{6 \text{ kJ/mol}}{8.31(\text{J/mol}^\circ\text{K})(273^\circ\text{K})^2} (10^\circ\text{K}) \\ &= 0.097. \end{aligned}$$

For salt, this is about equal to 18 g of NaCl per 100 g of  $\text{H}_2\text{O}$ . This result is useful for revising the first two product specifications given above.

Developing a basis that is similarly useful for the third, corrosion-based specification is more difficult. The corrosion rate will normally involve two or more sequential chemical steps. In the limit where surface chemical reactions are controlling, the rate of corrosion will be given by the Butler-Volmer equation, which for small overpotential  $\eta$  is

$$j_1 = j_0 \eta \mathcal{F} / RT,$$

where  $j_0$  is the exchange current density, that is, the reaction rate at equilibrium, and  $\mathcal{F}$  is Faraday's constant. Note that the corrosion rate is a flux, with units of moles per area per time. Unfortunately, we have no easy ways of guessing either  $j_0$  or  $\eta$  in this situation, so this result does not help us in our revision.

We can estimate the fastest possible corrosion rate, which will occur when paint or rust limits how fast the deicing chemical can reach the surface. This rate is the diffusion controlled limit:

$$j_1 = \left(\frac{D}{\delta}\right)c_1,$$

where  $D$  is the diffusion coefficient of the chemical across a rust layer of thickness  $\delta$ . Note that  $c_1$  is the molar concentration, not the mass concentration. Similarly, in the freezing point depression, the important variable was the molar concentration.

We can now compare the expected performance of the three possible chemicals. Although salt and urea are straightforward, CMA requires some explanation. This material, which is not readily available commercially, is made by reacting dolomite limestone and acetic acid:



The limestone sells for around \$20/ton; the acetic acid is about \$0.37/lb; so the material cost is almost \$800/ton. Clearly, this cost is dominated by the acetic acid and can be reduced if waste acetic acid is available.

The results of the comparison of salt, urea, and CMA are given in Table 2.4–1. Right away, we see that salt will be difficult to beat if the initial specifications are

Basic Compound	NaCl	Urea	CMA
Solubility g/100 g H <sub>2</sub> O	36	100	40
Species in solution	Na <sup>+</sup> , Cl <sup>-</sup>	$\text{O}=\text{C} \begin{matrix} \text{NH}_2 \\ \text{NH}_2 \end{matrix}$	Ca <sup>++</sup> , Mg <sup>++</sup> 4CH <sub>3</sub> COO <sup>-</sup>
Molecular weight	58.5	60	300
Moles particles/mole compound	2	1	6
Mole fraction at saturation	0.18	0.23	0.13
Moles particles/mass compound	34	17	20
Cost per metric ton, U.S. dollars	20	130	800
Moles particles per dollar	1700	130	25

*Note:* Sodium chloride is the benchmark. Urea is sometimes used on airport runways because of reduced corrosion. CMA ((CH<sub>3</sub>COO)<sub>4</sub> CaMg) is one alternative favored by some government agencies.

used. In particular, the first specification says that an alternative chemical should melt ice over a similar temperature range to salt. From the equations above, we see that the maximum freezing point depression is proportional to the maximum mole fraction, that is, the mole fraction of saturation. From Table 2.4–1, we see that these mole fractions are roughly comparable, so we seem to be on the right track.

However, the second specification is that a fixed mass of chemical should melt the same amount as salt. Here, the alternatives stumble. Although urea has a similar molecular weight as salt, it does not ionize, so a mass of urea gives a solution whose mole fraction is about half that of salt. In the same way, CMA produces only half the mole fraction as salt, or in the terms used in the table, 20 versus 34 particles per mass. Salt is better.

The third specification, regarding corrosion, is the hardest to evaluate. The corrosion from urea will be modest, because urea does not produce ions. Salt and CMA do produce ions. When corrosion is diffusion controlled, the corrosion rate is proportional to the ionic concentration. But ice melting is also proportional to ionic concentration. Thus any ionic chemical will accelerate corrosion and melt ice in roughly proportional amounts.

Finally, we turn to chemical cost. Although cost was not included in our original specifications, it will certainly have a role in our final decision. What will matter is the ice melted per dollar spent, or in chemical terms, the particles delivered per dollar spent. As Table 2.4-1 shows, salt is way out in front.

Thus if we still seek an alternative chemical, our specification requires significant revision. The exact nature of this revision depends on getting additional information. Even without this, we can see alternatives requiring creative thinking. For example, we are immediately struck by the high cost of the alternative chemicals. Urea is already a commodity, so we are unlikely to be able to cut its cost much. On the other hand, CMA's price is dominated by the acetic acid cost. To cut this cost, one group creatively fermented a mixture of lime and garbage in cement mixers that normally sat unused in the winter. They then used the fermented garbage as a deicer, a solution better suited for rural areas.

As a second example, we can remember that our real objective is to clear the road, not necessarily by melting the ice. If we can just get the ice to debond from the road surface, then we can remove it with a snowplow. This suggests replacing the specification of ice melted per mass of chemical with ice removed per mass in some standard test. Such a revised specification makes good sense.

#### **EXAMPLE 2.4-2 SCRUBBING NITROGEN FROM NATURAL GAS**

In the next few decades, a major fraction of the world's energy is expected to come from natural gas. The best natural gas is largely methane, with small amounts of other hydrocarbons. Future natural gas may be much less pure, containing large amounts of carbon dioxide and nitrogen.

These impurities have to be removed. One easy way is cryogenic distillation, but this is prohibitively expensive. Carbon dioxide can be removed by absorption into aqueous solutions of amines, using packed towers like that in Figure 2.4-1. There is no similar method of absorption for nitrogen.

Thus the need is for a liquid or liquid solution that absorbs nitrogen but not methane. There is currently no liquid with this property, so there is no obvious benchmark. Instead, we choose monoethanol amine, the standard absorbent for carbon dioxide. Our first attempt at product specification seeks a new liquid solution for nitrogen that would be used as the amine solutions are used for carbon dioxide. This new solution would have similar loading, react with similar kinetics, and use similar equipment to that used for CO<sub>2</sub>. Such similarity is sometimes called a "transparent technology" because the operator running the process does not need to know if he or she is removing CO<sub>2</sub> or N<sub>2</sub>.

See if these specifications are reasonable, and revise them if necessary.

#### **SOLUTION**

We can begin by looking at the stoichiometry and the mass balances for carbon dioxide. The key reaction is



where R is, for example, HOCH<sub>2</sub>CH<sub>2</sub>. If the aqueous solution contains 10 wt.% amine and reacts completely, then the amount of CO<sub>2</sub> absorbed will be

$$(10\%) \left( \frac{1 \text{ mol CO}_2}{2 \text{ mol amine}} \right) \left[ \frac{44 \text{ g CO}_2/\text{mol}}{61 \text{ g amine/mol}} \right] = 3.6\% \text{ CO}_2.$$

To meet our specifications, we would like our new liquid to absorb a similar amount of nitrogen.

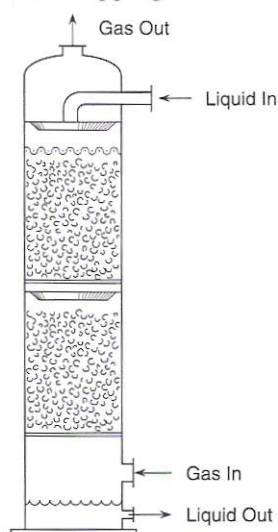
To see if this specification is reasonable, we need to anticipate the chemistry of nitrogen complex formation. The complexes are most likely going to be organometallic, possibly with a porphyrin structure aping that in hemoglobin. These chemical compounds are large, with a molecular weight around 500 or more. They are very unlikely to be soluble in water to greater than 10 wt. %. Thus, if the organometallic compound forms a 1:1 complex,

$$10\% \left( \frac{1 \text{ mol N}_2}{1 \text{ mol complex}} \right) \left[ \frac{28 \text{ g N}_2/\text{mol}}{500 \text{ g complex/mol}} \right] = 0.6\% \text{ N}_2.$$

Like it or not, the nitrogen scrubbing solution is going to be more dilute.

Justification for the 10 wt. % figure as the likely limit we will be able to achieve for the solubility of our nitrogen absorbing complex comes from animals' oxygen absorbing systems. Animals without corpuscles achieve pigment concentrations in their blood of up to about 5 wt.%. Red corpuscles allow pigment concentrations in the blood stream to be raised above this figure (it is about 15 wt. % in human blood), making high levels of aerobic activity sustainable. See Figure 2.4–2 for examples of the oxygen absorbing capacity of animals. Squid have no blood corpuscles; they are therefore vulnerable to predation by fish, which are equipped with corpuscles. To compensate, squid have three hearts in order to speed up their circulation, and adaptations such as ink release to confuse predators. The evolutionary pressure to maximize the oxygen carrying capacity of blood has been strong. We are most unlikely to be able to develop a heme analog with a higher nitrogen carrying capacity; if anything, 10 wt. % represents an optimistic value.

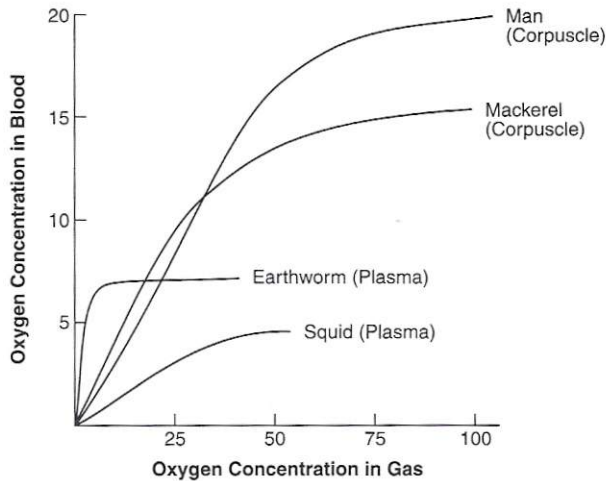
The relative dilution of our absorber, a consequence of reaction stoichiometry, has a significant effect on the rates of absorption as well. There are two types of rate processes that are important. First, the new complex must react with the nitrogen quickly and reversibly. Ideally, we would like complex formation to be as fast or faster than the amine-CO<sub>2</sub> reaction. Equally, we would like to have the complex quickly decompose when we increase the liquid temperature slightly. To discover if this can happen, we must synthesize our complexing agent and make absorption and desorption experiments. The results of these experiments will determine the height of the packed towers that we will require for absorption and stripping.



**Figure 2.4–1. Packed Towers for Carbon Dioxide Adsorption.**

The gas containing carbon dioxide flows upward, and an aqueous solution of reactive amines flows countercurrently downward. The reaction facilitates the removal of the carbon dioxide.





**Figure 2.4-2. The Oxygen Absorbing Capacity of Various Animals' Blood.** Animals without red blood corpuscles, like the squid, achieve substantially lower oxygen loading at saturation than those with corpuscles, like the mackerel. Units are mol O<sub>2</sub> in 100 mol of blood and mm Hg partial pressure of O<sub>2</sub>.

The second type of rate process concerns not the height but the diameter of the packed tower. To explore this, we return to our carbon dioxide benchmark. Imagine that we have a gas flux  $G$  of density  $\rho_G$  and a liquid flux  $L$  of density  $\rho_L$  flowing in a packed tower of cross section  $A$ . As a basis, we assume that we have a total gas flow equal to 100 mol/min. This feed stream contains 80 vol. % CH<sub>4</sub> and 20 vol. % CO<sub>2</sub>. Such a feed will have an average molecular weight of 21.6 g/mol. If 90% of the CO<sub>2</sub> is removed to produce an amine solution which is 50% saturated, then the mass flow of amine solution  $LA$  may be found from

$$\begin{aligned} (\text{mass CO}_2 \text{ leaving in liquid}) &= (\text{mass CO}_2 \text{ absorbed from gas}), \\ 0.50(0.036)LA &= 0.90(0.20) \frac{100 \text{ mol}}{\text{min}} \left( \frac{44 \times 10^{-3} \text{ kg}}{\text{mol}} \right), \\ LA &= 44 \text{ kg/min}. \end{aligned}$$

The operation of the packed tower depends critically on the "flow parameter," which for this feed is

$$\begin{aligned} \frac{LA}{GA} \sqrt{\frac{\rho_G}{\rho_L}} &= \frac{44 \text{ kg/min}}{(100 \text{ mol/min})[(0.0216 \text{ kg/mol})]} \sqrt{\frac{21.6 \text{ g}/22.4 \times 10^3 \text{ cm}^3}{1 \text{ g/cm}^3}}, \\ &= 0.63. \end{aligned}$$

This value, in the middle of the normal design range, can be used to determine the tower's cross-sectional area.

We now turn from the benchmark, carbon dioxide, to our new target, nitrogen. As before, we imagine that we have the 100 mol/min feed, which is now 80% CH<sub>4</sub> and 20% N<sub>2</sub>, and 90% of the N<sub>2</sub> is removed to produce a liquid that is again 50% saturated. The mass flow of this new product solution is

$$\begin{aligned} 0.50(0.006)LA &= 0.90(0.20) \frac{100 \text{ mol}}{\text{min}} \left( \frac{28 \times 10^{-3} \text{ kg}}{\text{mol}} \right), \\ LA &= 170 \text{ kg/min}. \end{aligned}$$

Now the flow parameter is quite different:

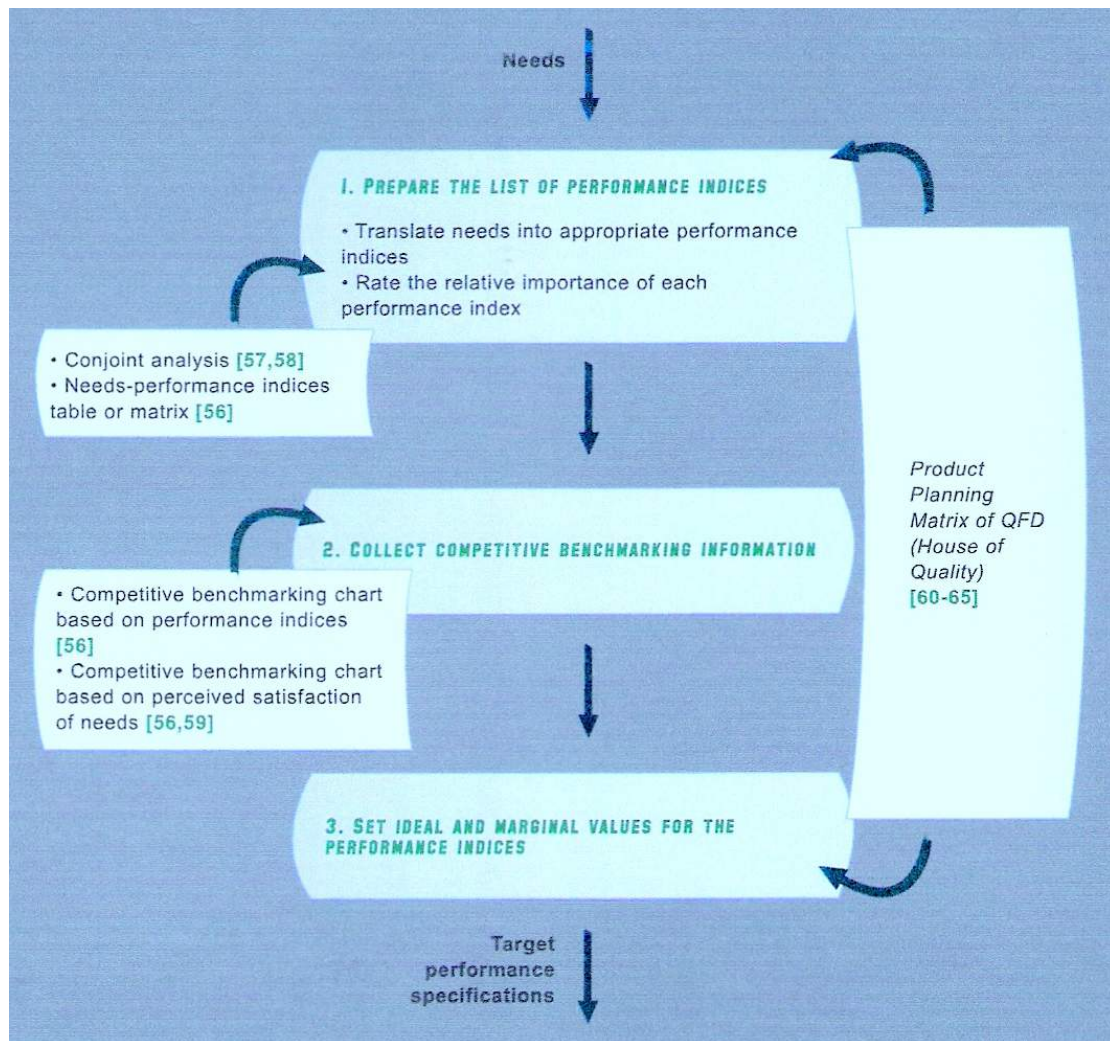
$$\frac{LA}{GA} \sqrt{\frac{\rho_G}{\rho_L}} = \frac{170 \text{ kg/min}}{(100 \text{ mol/min}) [(0.0184 \text{ kg/mol})]} \sqrt{\frac{18.4 \text{ g}/22.4 \times 10^3 \text{ cm}^3}{1 \text{ g/cm}^3}},$$
$$= 2.6.$$

This value is higher than the normal design range, and it may require packed towers of larger cross sections than used for the amines.

Thus the original specification, that the absorption of nitrogen closely imitate that of carbon dioxide, will be difficult to achieve. Because complexing the nitrogen will require a complex of high molecular weight, the nitrogen concentration in the absorbing liquid will be less than that for the carbon dioxide. This means that relatively more liquid will be needed to remove the nitrogen, which in turn suggests that the packed tower geometry will change. This is by no means a fatal flaw for nitrogen absorption. It does mean that the specifications for the two absorptions will be different.

Shematski prikaz postavljanja specifikacij produkta:

Vir: [http://www.engsc.ac.uk/an/mini\\_projects/cpd/index.html](http://www.engsc.ac.uk/an/mini_projects/cpd/index.html) (6.9.2011)



Primer postavljanja specifikacij produkta: Prenosni hladilni sistem za pijačo:

Vir: [http://www.engsc.ac.uk/an/mini\\_projects/cpd/index.html](http://www.engsc.ac.uk/an/mini_projects/cpd/index.html) (6.9.2011)

Če po preverjanju specifikacij produkta bistvene spremembe niso potrebne je naslednja faza iskanje idej za nov produkt. Pred tem pa je potrebno ugotoviti ali so specifikacije produkta v skladu s poslovno strategijo organizacije. Zato se na tem mestu vedno vprašamo ali je smiselno nadaljevati z razvojem novega produkta ali ne, tudi če so preliminarne specifikacije dobre. Zavedati se je potrebno, da bodo vsi nadaljnji koraki v razvoju novega produkta zahtevnejši, dolgotrajnejši in bistveno dražji. Če nadaljnji razvoj konkretnega produkta ni perspektiven, je smiselno, da se projekt (načrtovanje novega produkta) čim prej zaključi.

Jedro projektnega team-a ob zaključku faze "Potrebe" pripravi prvo fazno pisno poročilo in prvo fazno ustno predstavitev aktivnosti in rezultatov projekta. Na predstavitvi navadno sodelujejo tudi vodilni iz managementa organizacije. Po predstavitvi mora pasti odločitev ali se delo na projektu nadaljuje.