EXAMPLE 5.2–1 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 is a very effective insulator. The properties of this insulation have been used to establish standards for home refrigerators. The external dimensions of refrigerators have become standard, so a new refrigerator will fit into the space

Table 1 ***Properties of gases used in insulating foam*** Freon's large diameter and high molecular weight give it the lowest thermal conductivity.

	Molecular weight, daltons	**Molecular diameter, Å**	**Boiling point, °C**
Nitrogen (N_2)	28	3.8	–196
Carbon dioxide (CO_2)	44	3.9	–79[a]
Freon12 (CCl_2F_2)	121	5.3	–30

[a] Sublimes.

occupied by the old one. The internal dimensions have also become standard, so that milk bottles fit conveniently inside. The insulation required for energy efficiency is 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 which 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 like hair sprays. Nonetheless, the freon in foam will eventually leak out, perhaps long after the refrigerator has been scrapped. The manufacture of polyurethane foam blown with freon is being phased out, as a consequence of increasing regulatory restrictions.

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 in any refrigerator 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

$$k_T = \frac{0.08}{\sigma^2\Omega}\sqrt{\frac{T}{\tilde{M}}}$$

where σ is the molecular diameter, in Å; Ω 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 5.2–1

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

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

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.

We need a better foam. A careful search for ideas has produced many interesting alternatives, including materials made of many layers of aluminum 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 which make the product active. In this case, there is no chemical trigger, 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 central product 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

$$k_\mathrm{T} = \frac{1}{3}\begin{bmatrix}\text{distance between}\\ \text{collisions}\end{bmatrix}\left[\frac{\text{energy}}{\text{volume}}\right]\left[\frac{\text{volume}}{\text{area} \times \text{time}}\right]$$

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:

$$\frac{1}{2}mv^2 = k_\mathrm{B}T$$

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 the molar heat capacity $\widetilde{C}_V$, is given by

$$c[\widetilde{C}_V] = \frac{p}{k_\mathrm{B}T}\left[\frac{3}{2}k_\mathrm{B}\right]$$

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 λ that a gas molecule travels before it collides with a second gas molecule. This mean free path is related to the volume per molecule:

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

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

$$k_T \propto \frac{1}{\sigma^2}\sqrt{\frac{T}{m}}$$

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

This large-bubble result is dramatically different to 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

$$k_T = dp\sqrt{\frac{k_B}{2mT}}$$

where d is the bubble diameter. Note how different this result is from the previous equation. While 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 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 λ and the bubble diameter d:

$$\begin{aligned}Kn &= \frac{\lambda}{d}\\ &= \left(\frac{4}{\pi}\right)\frac{k_B T}{p\sigma^2 d}\end{aligned}$$

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. While we can try to make these mechanically, we will find it difficult to get bubbles smaller than 1 μm, 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 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 CO_2 that slowly diffused through the foam to react. It turns out that a chemical trigger is involved in our product manufacture after all.

The result is a foam initially the same as any other CO_2-blown foam, but which gets to be a better insulator with time. Eventually, as the gas pressure gets lower and lower, the foam conducts even less 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 will be exceeded.