

*The hair of the dog that bit you*  
Ancient proverb

# 2

1005

## Introduction: Carbon dioxide

### 2.1 The chemical industry

Industrialized societies depend on chemicals. In this discussion I define chemicals as pure substances that are produced by industry for industry. Chemicals might be used in the processing of products, or blended with other chemicals in formulations that might be sold to users as products. As a familiar example, sugar is produced by the sugar industry. It is a pure substance (sucrose), and it is mostly used in the industry as an ingredient for processed food: even the sugar that gets bought by consumers are not eaten raw but added to food. <sup>To do (1)</sup>

The chemical industry produces a huge variety of products, anything from something as simple as sulphuric acid to something as sophisticated as medication. All of these chemicals help produce the products found necessary in industrialized societies. Nevertheless, the chemical industry is not held in high regard by people outside industry. <sup>To do (2)</sup>

A part of this negative perception comes from the chemical industry's reputation for pollution. It pains me to say that this reputation is not undeserved.

In 1984 a gas leak at a chemical plant in Bopal, India, caused the death of thousands of people, and the injury of thousands more <sup>To do (3)</sup>. The ozone layer over Antarctica is slowly recovering from depletion caused by the reckless emissions of chlorofluorocarbons <sup>To do (4)</sup>. Plastics microparticles are now found everywhere in the oceans <sup>To do (5)</sup>, and the pesticide DDT is found in the breast milk of Inuit mothers. <sup>To do (6)</sup>

The chemical industry is also a prodigious producer of greenhouse gases. Apart from the carbon dioxide emitted by the production of energy for chemical processes, some chemical processes emit carbon dioxide as a waste product. One of the most notable of these is the reduction of atmospheric nitrogen as the first step in the production of nitrogen fertilizers. Of all the greenhouse gases monitored by the IPCC, only carbon dioxide, methane and nitrous oxide are found in nature: the others are exclusively products of the chemical industry. <sup>To do (7)</sup>

While it is true that these impacts were caused by human negligence or ignorance, and not by the chemicals themselves, which are well-behaved when they are used in controlled environments, the moral response must be to look at the intrinsic safety of chemicals.

### 2.1.1 “Green chemistry”

1040 The date of the birth environmental movement is conventionally set to 1962, when the biologist Rachel Carson published the book *Silent Spring*, which pointed out the destruction of nature by the unrestricted use of pesticides, and the dangers of overuse. This was a direct imputation of the chemical industry, because the pesticide products contained many chemicals.

1045 Chemists are human, and the realization that chemicals can have detrimental effects brought at least some chemists to reflect on their own work. This has given rise to the concept of *green chemistry*. Although the term has no rigorous definition or quantitative measure(Linthorst 2010), a set of 12 principles or guidelines are proposed:

1. It is better to prevent waste than to treat or clean up waste after it is formed.
- 1050 2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 1055 4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- 1060 6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
- 1065 8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
- 1070 11. Analytical methodologies need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.
- 1075 12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

While these guidelines are clearly written with synthetic chemistry in mind, it does not mean that they do not apply to analytical chemistry. Item 7 suggests that,

when possible, one should use hydrogen rather than helium as mobile phase in capillary gas chromatography: hydrogen is renewable, whereas there is only a finite amount of helium available.

One large area of the greening of chemistry is changing the use of solvents. Solvents play a large role in everyday chemistry, but most solvents used in chemistry are ultimately derived from petroleum, and most are toxic to some degree.

One application for solvents is extractions. Extractions can be either from a solid material, as in extracting aspirin from willow bark, or liquid-liquid, where a compound is extracted from one liquid into another.

A good bit of work is being done to create new solvents to replace existing ones.<sup>To do (8)</sup> But there are a few solvents that are already “green”, such as water or ethanol.

One such naturally green solvent is carbon dioxide.

### 2.1.2 Carbon dioxide as a green chemical

Carbon dioxide as a chemical is used in industry in a few key areas.

- Carbon dioxide is often used in firefighting, in the form of portable fire extinguishers, or room flooding systems. In this last use it is displacing the ozone-depleting halomethane (Halon).
- When liquid water is supersaturated with carbon dioxide, the gas escapes slowly in the form of streams of tiny bubbles. This phenomenon makes beverages prepared from water supersaturated with carbon dioxide (or *carbonated water*) interesting to drink, and a large, international industry is based on carbonated water.
- Carbon dioxide has a freezing point of  $-77^{\circ}\text{C}$ , and the solid can be conveniently obtained by evaporating liquid carbon dioxide at atmospheric pressure. The evaporating liquid rapidly cools the stream of carbon dioxide, lowering the temperature of the stream to below the freezing point, and the gas crystallizes into the solid. The resulting ‘snow’ can be compressed into blocks, which only slowly sublimates into gaseous carbon dioxide. Packing frozen food products together with this ‘dry ice’ allows for it to be transported cold,
- Pellets of dry ice can be entrained in a jet of air, and used to abrade surface for cleaning (Spur, Uhlmann, and Elbing 1999). This use of carbon dioxide can displace toxic solvents and/or abrasives dust.
- Carbon dioxide is a ‘natural refrigerant’ (Pearson 2005), and can be used to displace hydrofluorocarbon refrigerants, which are potent, long-lived greenhouse gases.
- Carbon dioxide can be used as a preservative and anti-oxidant in packaged food. If headspace air in a packaged food is removed by purging it with carbon dioxide, the growth of microbes can be discouraged, extending the shelf life of the product (Jacobsen and Bertelsen 2002).
- Carbon dioxide can be used to extract compounds from natural products.

Of these uses, extractions are economically the most important.

## 2.2 Extractions using carbon dioxide

### 2.2.1 Commercial extractions

There are several commercial processes that use

#### Plant oils

1125 Vegetable oils are obtained from various crops, and are can be extracted from the substrate by pressing, heating or extraction. High-pressure carbon dioxide has been used to extract vegetable oils.

#### Hops

1130 Hops is an essential component in the brewing of beer. It imparts a desired bitter flavour, stabilizes the beer during storage, and assists with foam formation (Schönberger and Kostecky 2011). Hops is a seasonal crop with a limited growing range, but the demand for beer is not limited to certain areas or seasons. The creation of hops extract makes it possible to have the benefit of hops without owning a hops plantation or storing and transporting dried hops over long distances. All hops ex-  
1135 tracts produced today are extracted by carbon dioxide (Hunt et al. 2010).

#### Coffee

Coffee is an international industry, with coffee drunk in many cultures and in many forms. One of the attractions of coffee is the effects of the psychoactive substance, caffeine. Caffeine is a mild stimulant and promotes wakefulness. A small propor-  
1140 tion of coffee drinkers enjoy drinking coffee, but prefer to avoid the stimulant effect, which might induce insomnia. For these coffee drinkers the market supplies decaf-  
feinated coffee.

Given the large amount of coffee traded (an estimated 167.47 million bags of coffee in the 2018-2019 coffee year (*Coffee Market Report December 2018 2018*))<sup>1</sup>, if only  
1145 a small percentage of coffee needs to be decaffeinated, it will be a large amount of coffee to process, and industrial processes will be necessary to supply the demand.

Decaffeination of coffee is achieved by selectively extracting the caffeine from green (*i.e.* unroasted) coffee beans using carbon dioxide. This is the largest use of carbon dioxide for extraction (Ramalakshmi and Raghavan 1999). The extracted  
1150 caffeine is sold for use in medication and cold drinks.

### 2.2.2 Analytical Extractions

The first extractions using carbon dioxide was of course not aimed at developing an industrial operation, but to develop a method for analytical chemistry. This method is usually called SFE, for supercritical fluid extraction.

### 1155 2.2.3 Why carbon dioxide?

But what makes it better than any other solvent?

There are two aspect to this question. The first is about the *greenness* of carbon dioxide. It is non-toxic, non-persistent, non-flammable, non-corrosive, inexpensive,

<sup>1</sup>The factoid that “coffee is the second-most traded commodity after oil” has been proven to be untrue.(Greenberg 2017)

commercially available, and a waste product. (It goes without saying that this carbon dioxide is sourced from a carbon-neutral source, perhaps the brewery industry.)

The second aspect of the desirability of carbon dioxide lies in its physical properties and the conditions under which we use it.

Chemists will intuitively understand that gaseous carbon dioxide has no solvating properties, and that liquid carbon dioxide should not behave much differently than any other solvent. Both these statements are true under 'normal' circumstances.

Consider the case of an isobaric cooling of a volume of gas. The gas-liquid transition takes place because energy is removed from the system. At some point the kinetic energy of some of the molecules becomes less than the energy of the intermolecular forces, and the molecules prefer to clump together. The remaining gas molecules receive the excess energy, and therefore stay in the gas state, until more energy is removed.

Now consider a solute (solid or liquid) in the same volume of gas being cooled. In this case, as the gas cools the gas-solute intermolecular forces can become more important in the gas-gas interaction at a temperature which is higher than the boiling point. In such a case the gas will have solvating properties, and the solute will become truly dissolved in the gas.

The same argument follows during the isothermal compression of a gas.

If there are more than one solute in the volume of gas, some might dissolve in the gas, while others one might not. This means that the solvating gas can be *selective*. It can also be seen that the solvating power of the gas will depend on the temperature and the pressure of the gas. This means that the solvent becomes *tunable*.

While the compressed gas has solvating properties, it still has the physical properties of a gas:

**Diffusivity** The solvating gas maintains its low diffusion coefficient, which means that it can easily diffuse into porous material, and that solutes will rapidly diffuse through it.

**Surface tension** The solvating gas has a low surface tension, which means that it will readily 'wet' surfaces and penetrate porous material.

**Viscosity** The solvating gas has a low viscosity, which means that it takes little energy to pump it.

For historical reasons, such solvating gases are known as a 'supercritical fluids', because they are usually obtained by heating a liquid at high pressure, so that the temperature and pressure of the substance is higher than its *critical point*. The critical pressure of a substance is the pressure above which it is impossible to create a gas-liquid phase transition by isobaric cooling, and the critical temperature is the temperature above which it is impossible to create a gas-liquid phase transition by isothermal compression. When the gas is at its critical temperature and critical pressure, it is at its critical point. The critical point is very different from the *triple point*: there is no equilibrium involved. (See figure 2.1.) The terms 'supercritical fluid' and 'dense gas' are synonymous — the term 'dense gas' of course implies that the gas behaviour is far from that of an ideal gas.

To do (12) in practice, near the critical point there are only very small differences between the properties of the liquid and the gas, so that many separations that are done below supercritical temperature but at high pressure.

The critical pressure of carbon dioxide is 304.12 K (31.10 °C) , and the, critical pressure is 7.39 MPa (72.9 atm). This temperature and pressure are easy to achieve

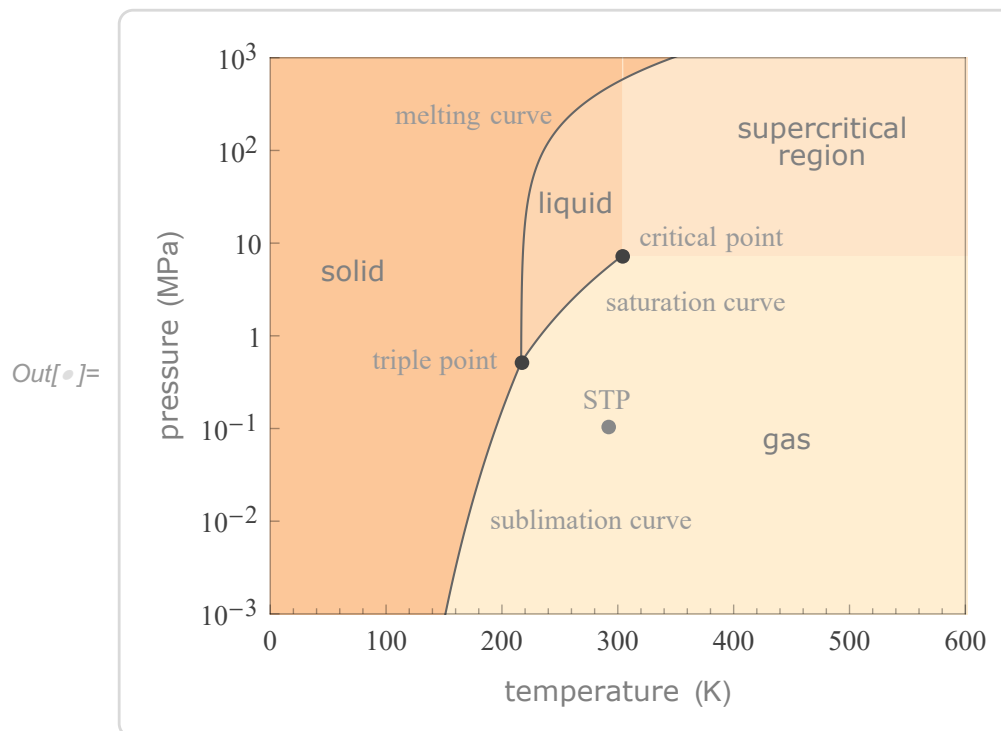


FIGURE 2.1: The phase diagram of carbon dioxide

in the laboratory with standard chromatographic instrumentation, or indeed in an industrial plant with using process engineering technologies.

Carbon dioxide is gaseous at ambient conditions. This means that once it has been used in its role as extractant, and it is exposed to the atmosphere, it will rapidly evaporate, without needing added heat, and leaving no residues.

The practical alternatives to carbon dioxide as a supercritical fluid are ammonia, methanol, CFCs/Freon, hydrocarbons (propane, butane), water and sulfur hexafluoride. All of these lack green attributes: hydrocarbons pollute, the CFCs deplete ozone, sulfur hexafluoride is a potent greenhouse gas, and methanol and water are liquid at ambient conditions.

For these reasons the term supercritical fluid is practically synonymous with high-pressure carbon dioxide.

It is also possible to use supercritical fluids as . This topic falls outside the scope of this discussion.

### Modifiers

While the solvating power of a supercritical fluid is certainly 'tuneable' by adjusting its pressure and/or temperature, the range in solubility might be quite limited in practice. Supercritical carbon dioxide is quite non-polar, with a polarity ascribed to it similar to that of dichloromethane, although the reality is more complex. To do (13)

Just as with other solvents, it is possible to add a co-solvent or *modifier* to the supercritical carbon dioxide. This makes it possible to increase the solubility of polar compounds in the supercritical fluid. Methanol, ethanol, formic acid and water are examples of suitable green modifiers for carbon dioxide.

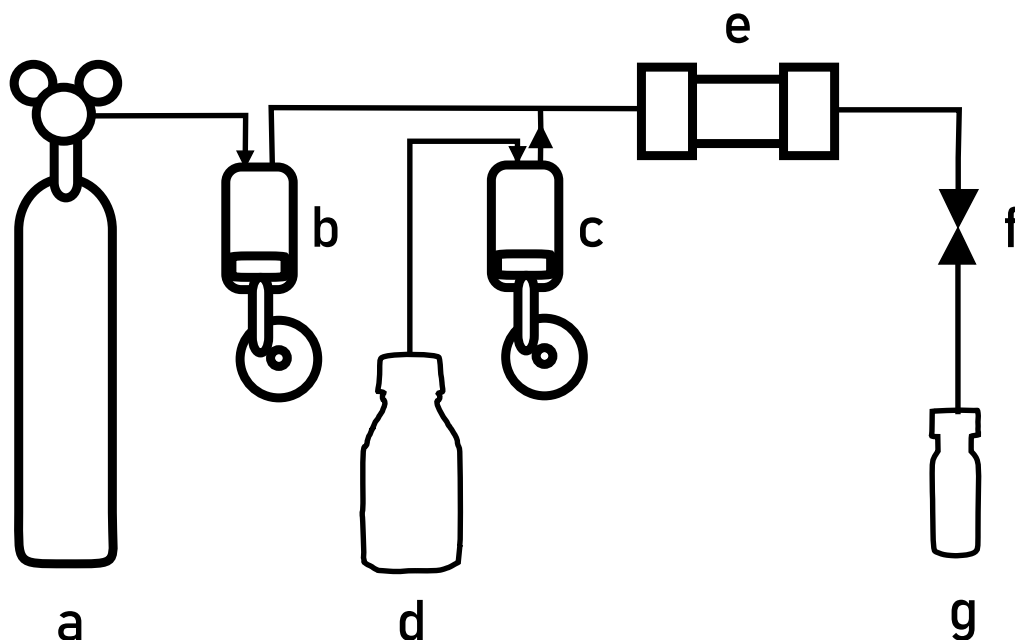


FIGURE 2.2: A diagram of an SFE system. (a) CO<sub>2</sub> supply (b) High-pressure SF pump (c) High-pressure modifier pump (d) Modifier reservoir (e) Extraction cell (f) Pressure control (g) Collection vessel

1230 When modifiers are used the carbon-dioxide, modifier and solute forms a ternary system, which can become difficult to model. While this is a challenge for process engineers who need to design efficiently industrial systems, analytical chemists can afford to be pragmatic and use heuristics to find suitable conditions.

### Practical extractions

1235 Figure 2.2 shows a schematic diagram of a system set up for supercritical fluid extractions.

To do (14) To do (15)

Carbon dioxide is readily available from suppliers of industrial gases, and high-purity grades are available. High-pressure pumps are used to compress the carbon dioxide and the modifier, which are mixed together at the appropriate ratio. The mixture gets pumped into the extraction cell, which contains the material that needs to be extracted. Having extracted the analyte from the material, the supercritical fluid passes through a pressure-control mechanism. This allows the pressure of the supercritical fluid to drop to ambient, turning it into a low-density non-solvating gas. The analyte becomes desolvated, and precipitates in the collection vessel.

#### 2.2.4

## 2.3 SFC

Solvents used in extractions can also be used

### 2.3.1 SFC and FID

1250 **To do...**

- ☐ 1 (p. 21): Cite sugar uses
- ☐ 2 (p. 21): cite perceptions of chemical industry
- ☐ 3 (p. 21): cite Bhopal
- ☐ 4 (p. 21): Cite ozone layer
- 1255 ☐ 5 (p. 21): autocite microplastics
- ☐ 6 (p. 21): autocite DDT
- ☐ 7 (p. 21): autocite AR4
- ☐ 8 (p. 23): autocite new green solvents
- ☒ 9 (p. 25): diffusivity of CO<sub>2</sub>
- 1260 ☒ 10 (p. 25): surface tension of CO<sub>2</sub>
- ☒ 11 (p. 25): viscosity of CO<sub>2</sub>
- ☐ 12 (p. 25): I
- ☐ 13 (p. 26): autocite CO<sub>2</sub> polarity paper.
- ☐ 14 (p. 27): Add dip tube to CO<sub>2</sub> cylinder
- 1265 ☐ 15 (p. 27): Add heater to extraction cell