manufacture of 1,1,1-trichloroethane, etc., all vinyl chloride is used to produce polyvinyl chloride or copolymers of vinyl chloride and other monomers.

Polyvinyl chloride is used extensively in the building and construction industry, as piping, floor covering, and exterior surface, weather resistant, covering. It is used in the insulation of electrical wiring, in packaging as a film, in apparel as a coating on fabric to impart a supposedly improved esthetic appearance or more practically, for raincoats, etc. Polyvinyl chloride is used for water hoses, for tarpaulins (sometimes with a fabric backing), in some paints, and for many other purposes too numerous to describe in detail. Polyvinyl chloride is the single most important polymeric substance in use today.

Remarks: The alleged carcinogenicity of vinyl chloride illustrates that political influence of vociferous minorities can overwhelm the need for proper attention to scientific questions in deciding socially important issues. The facts are these: Humans exposed to vinyl chloride by skin contact at frequent intervals for long periods of time will sometimes develop a cancer—sarcoma of the liver. Experimental animals exposed to vinyl chloride vapor at fairly low concentrations will also develop liver sarcomas. The limited evidence of human exposure to vinyl chloride vapor strongly suggests that such exposure cannot produce liver sarcomas. Yet, without requiring any further scientific evidence, vinyl chloride antagonists in the United States were able to politically force the vinyl chloride industry to take the steps necessary to preclude worker exposure to vinyl chloride vapor—at costs reflected in otherwise unnecessary price increases.

Methyl Alcohol

Average annual production: 3.4 × 10⁹ kg; value in US$. 1 x 10⁹

Process: By direct synthesis using carbon monoxide and hydrogen to form methyl alcohol:

$$CO + 2H_2 \rightarrow CH_3OH$$

If mixed oxides of zinc, manganese, chromium, and aluminum are used as the catalysts, pressure of 300 atm at 300 °C is required. With a copper catalyst, a lower pressure of 75 atm suffices at 300 °C. Less by-product is formed at the lower pressures.

Uses: Small amounts of methyl alcohol are used directly as a solvent but most of the methyl alcohol produced is raw material for the manufacture of other compounds. These include formaldehyde (which see), acetic acid—by carboxylation, methyl tertiary butyl ether, dimethyl terephthalate, methyl methacrylate, and methyl derivatives such as the amines and the halides. As a blend with tertiary butyl alcohol methyl alcohol has some promise as an octane booster in gasolines.

Remarks: The carbon monoxide and hydrogen raw materials are obtained from synthesis gas, a mixture of carbon monoxide and hydrogen in approximately the correct proportions for methyl alcohol synthesis. Synthesis gas is obtained by treating methane or other hydrocarbons (for example, the heavy hydrocarbon residues from petroleum refining) with carbon dioxide and water at 800 °C in the presence of a nickel catalyst. When properly controlled, the major products are carbon monoxide and hydrogen.

In the synthesis of methyl alcohol the major by-products are dimethyl ether and higher alcohols.

Methyl tertiary butyl ether is used primarily as an octane booster in gasolines. It is also used in laboratories in place of the more common ethers, diethyl ether and isopropyl ether, because, unlike these ethers it has little tendency to form ether peroxides on standing in the presence of air. Since ether peroxides are quite unstable and detonate occasionally with only a slight touch or impact, the use of methyl tertiary butyl ether as a solvent in laboratory work can be expected to increase.

Methyl alcohol is an intoxicant and is found in trace amounts in all fermented and even in distilled alcoholic beverages. When present in larger amounts by deliberate addition, it causes blindness and even death when ingested.

Acetone

Average annual production: 1 × 10⁹ kg; value in US$. 7 x 10⁸

Process: Acetone is one product from the peroxidation of cumene (see Phenol); it is also manufactured by the catalytic dehydrogenation of isopropyl alcohol using a brass or copper catalyst and 3 atm pressure at 500 °C. By-product hydrogen is recovered, acetone distilled off, and unreacted alcohol recycled.

Uses: To some extent directly as a solvent, for example in the manufacture of acetate rayon, but largely as a raw material for the manufacture of derivatives. Some derivatives are useful as solvents themselves, and as precursors also: methyl isobutyl ketone, methyl isobutyl carbinol, diacetone alcohol. Acetone is a raw material for the manufacture of methyl and higher methacrylates and of some pharmaceuticals.

Remarks: Acetone is another of the few chemicals involved in recent geopolitical history. Cellulose nitrate is an explosive and is used as "smokeless powder". Its manufacture during World War I required large amounts of acetone as a solvent. At that time, the major source of acetone was from the destructive distillation of wood. The requirements for acetone were so great in England in 1915–1916 that English forests were almost exhausted. Without the wood, black powder, a militarily much less desirable explosive, would have to be substituted. Through the efforts of the editor of the *Manchester Guardian* newspaper, David Lloyd George, England's Prime Minister, asked a young chemistry professor at the University of Manchester if he could find a solution. In less than three weeks he found another source: the controlled fermentation of corn starch. Refusing a proffered knighthood, the professor gained the promise of an unspecified favor to be granted later. By late 1917, a propitious time, the Foreign Secretary, Arthur James Balfour, promulgated the Balfour Declaration as the favor to the professor, Chaim Weizmann. Most historians agree that the Balfour Declaration was an essential

Average annual production: 2.7 x 10⁹ kg; value in US$: 5.5 x 10⁸

Process: Catalytic vapor phase oxidation of methanol, using mixtures of air and methanol. Silver or copper screen catalyst can be used, but a mixed outside catalyst (oxides of moiybdenum, iron, vanadium) gives better yields—at higher cost.

Uses: Formaldehyde is a raw material for the manufacture of a wide variety of compounds. These include urea formaldehyde resins, phenol formaldehyde resins, polyacetal resins, butanediol, hexamethylenetetramine, melamine formaldehyde resins, tetrahydrofuran, and polyols such as pentaerythritol and 2-ethyl-2(hydroxymethyl)-1, 3-propanediol.

The resins are partially copolymerized forms of their named components, used as adhesives, the resins are mixed with other solids (such as flakes of wood or other fibrous material) and the mixture heated under pressure. The resins then polymerize completely, binding the fibrous components to form a tough, durable structural material The other compounds mentioned above are themselves the starting points for a wide variety of still other useful compounds; note that most of these derivatives are characterized by two or more active functional groups, amine or hydroxy in the examples mentioned, which provide the means for the preparation of a variety of derivatives.

Remarks: The oxidation of methanol to formaldehyde can be thought of as involving two reactions, dehydrogenation to form formaldehyde, an endothermic process, and the oxidation of methanol to formaldehyde and other products, an exothermic process. For optimum formaldehyde production, the temperature should be about 500 °C; to achieve this, the ratio of air and methanol introduced into the reaction region is balanced so that the endo- and exothermic reactions, along with radiant heat loss, maintain the reaction region at the optimum temperature.

An alternate preparation of formaldehyde is the controlled oxidation of methane or higher hydrocarbons, the latter giving a variety of products that must be separated. This alternate is practical only when there is a good market for the other products.

Formaldehyde polymerizes readily to the trimer, trioxane, and to higher not as well characterized polymers. It is often sold as a monomer in water solution with methanol as an inhibitor to minimize polymerization Trioxane, however, readily "monomerizes" in the presence of acid.

Phenol

Average annual production: 1.2 x 10⁹ kg; value in US$: 5 x 10⁸

Process: The peroxidation of cumene (isopropyl benzene) yields both phenol and acetone as the major products, two steps are required:

$$C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5C(CH_3)_2OOH$$

The process requires a pH near neutrality and 110 °C, air supplies the needed oxygen. In the second step under acidic conditions, cumene hydroperoxide is decomposed into phenol and acetone. Other products include methylstyrene (sold or catalytically hydrogenated to cumene and recycled) and acetophenone (sold); unreacted cumene is recycled.

Uses: As a raw material for the manufacture of phenol formaldehyde resins (see Formaldehyde) Similarly, for the manufacture of bisphenol A (4,4'-isopropylidene diphenol) from phenol and acetone—used in resin manufacture. Similarly, for polycarbonate resins. Some alkyl derivatives of phenol can be used as surfactants. Phenol is used for the manufacture of adipic acid and of caprolactam, $NH(CH_2)_5CO$, both are precursors of nylon.

Remarks: The unique toxicity of phenol is not well-known—it is rapidly absorbed through the intact skin and unless the area of skin affected is quite small, the effect is known to be fatal within as little as two minutes. The remedy is *immediate* and *vigorous* rubbing *and* scrubbing under flowing water with a cloth pad for several minutes until all of the phenol has been rubbed and scrubbed away.

Alternate syntheses for phenol include brine and benzene as the raw materials. The brine is electrolyzed to chlorine and sodium hydroxide (which see); chlorine plus benzene with an iron catalyst forms monochlorobenzene (if controlled). The chlorobenzene reacts with sodium hydroxide to form phenol and sodium chloride, under acidic conditions. The sodium chloride is recycled to chlorine and sodium hydroxide, and so on. In the alkaline hydrolysis of chlorobenzene, diphenyl ether is the expected major side product. Its formation is minimized by the deliberate addition of diphenyl ether, an example of the application of Le Chatelier's principle.

Another alternate is the oxidation of toluene to benzoic acid followed by the oxidation of this acid in the presence of a copper catalyst to phenol and carbon dioxide. This synthesis is industrially useful only when the price of toluene is low and that of phenol high.

Cumene is formed by the catalytic addition of benzene to propylene Both are products from petroleum, often phenol plants are located near oil wells or shipping ports and are owned by the petroleum manufacturer.

Some phenol is obtained as a by-product of coke manufacture

Vinyl Chloride

Average annual production: 2.5 × 10⁹ kg; value in US$: 1.3 x 10⁹

Process: 1,2-dichloroethane (so-called dichloroethylene) is dehydrochlorinated using a charcoal or pumice catalyst at 3 atm and 500 °C. The product vinyl chloride is quickly quenched with cold 1,2-dichloroethane and then separated from the quenchant and from minor by-products by distillation

The 1,2-dichloroethane is itself produced in the same plant or in a separate but adjacent plant by the addition of chlorine to ethylene in the presence of 1,2-dibromoethane, using an aluminum chloride or iron (III) chloride catalyst at 50 °C.

Uses: Except for some very small uses as the raw material for the