INDUSTRIAL ORGANIC CHEMICALS

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To
Anthony Jacob, Bessie, David, Debbie,
Michelle, Ralph, Ted, and Virginia.

PREFACE

In the early 1970s, one of us (BGR) wrote a book celebrating the rapid growth of the adolescent chemical industry. The organic chemicals industry at the time was growing at four times the rate of the economy. It was indicated nonetheless that "trees do not grow to the sky." In 1980, in another book, we both declared the industry to be middle-aged with slow or zero growth. In this totally revised and expanded version of our earlier book, we reflect that the industry, at any rate in the developed world, is showing many of the illnesses of late middle-age.

The problems have arisen first from the undisciplined building of excess capacity with consequent fierce competition and low prices. Second, the entry of numerous developing countries into the industry has exacerbated the situation (Section 1.3.3), and third, there has been much stricter government legislation (Section 1.3.7). There is massive worldwide restructuring and continual shifting of commodity chemical manufacturing to areas other than the United States, Western Europe, and Japan. The Middle East and Southeast Asia are the principal new players in the game. Perhaps this trend will continue and the present developed world will in the future confine itself to the manufacture of specialties, but the economic and political forces at work are more complex than that. We hope to be able to discuss their resolution in another edition in about 10 years' time.

Meanwhile, some things have not changed. The organic chemicals industry is still based on seven basic raw materials all deriving from petroleum and natural gas. The wisdom of teaching about the chemical industry on the basis of these seven building blocks has been confirmed by the fact that, since the publication of our first book, one of us (HAW) has delivered by invitation 200 courses in 27 countries on the fundamentals of the industry based on this pattern. Most of these courses are for industrial personnel, but academia has not been neglected.

Furthermore, some changes have been positive. For example, there have been exciting new processes such as the development of metallocene catalysts (Section 15.3.12). Section 4.6.1 describes new methyl methacrylate processes that give a potentially cheaper product, that do not produce ecologically undesirable ammonium hydrogen sulfate byproduct or (in another process) that eliminate the use of dangerous hydrogen cyanide.

In this book, our main objective is still to present the technology of the organic chemicals industry as an organized body of knowledge, so that both the neophyte and the experienced practitioner can see the broad picture. Nonetheless, we have expanded its scope to include not only new processes but many apparently less important reactions that are significant because they give rise to the more profitable specialty chemicals. The lesser volume chemicals have been clearly delineated as such, and the reader who wishes to see the industry on the basis of its large tonnage products can omit these sections.

We hope this book will be useful both to college students who have studied organic chemistry and to graduates and industrial chemists who work in or are interested in the chemical industry. Even though much of the chemistry has remained the same, the change in the way the industry looks at its problems provides ample justification for our offering this volume as a fresh perspective on industrial organic chemicals.

Tarrytown, New York
London, England

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UNITS AND CONVERSION FACTORS

WEIGHT

thousand pounds	metric tons (tonnes or thousand kg)	long tons	short tons
1	0.4536	0.4464	0.5000
2.2046	1	0.9842	1.1023
2.2400	1.0160	1	1.1200
2.0000	0.9072	0.8929	1

VOLUME

liters (10^{-3} m^3)	cubic feet	US gallons	Imperial gallons
1	0.03532	0.2642	0.2200
28.32	1	7.481	6.229
3.785	0.1337	1	0.8327
4.546	0.1605	1.201	1

PRESSURE

atmospheres	bar	torr (mm Hg)	psi	kg cm^{-2}
1	1.01325	760	14.696	1.033
0.9869	1	750.06	14.504	1.020
0.001316	0.001333	1	0.01934	0.00136
0.06805	0.06895	51.715	1	0.0703
0.968	0.980	735.3	14.225	1

(1 bar = 10^5 pascal or newtons per square meter)

TEMPERATURE

Expressed as °C (= degrees Centigrade or degrees Celsius)

Degrees Fahrenheit (°F) = 1.8(°C) + 32

(°C) = 0.556(°F − 32)

Degrees Kelvin (°K) = (°C) + 273.15

0°K = − 273.15°C = − 459.7°F

HEAT

kilojoules	kilocalories	British thermal units (10^{-5} therms)
1	0.239	0.948
4.184	1	3.968
1.054	0.252	1

One tonne of oil is equivalent to

3.97×10^7 Btu
.01 teracalories
.042 terajoules

1.5 tonnes of coal (typical calorific value)
3 tonnes of lignite (typical calorific value)

0.805 tonnes of LNG
1111 m^3 of natural gas
39200 cubic feet of natural gas

12000 kWh of electricity

One cubic foot of natural gas = 1000 Btu
One m^3 of natural gas = 9000 kcal = 37600 kJ
One kWh = 3412 Btu = 860 kcal

NOBLE METALS

Noble metals—gold, silver, platinum, palladium, rhodium etc.—are traded in ounces. These are not the familiar avoirdupois ounces (= 28.35 g) but troy or apothecary ounces (= 31.15 g). One ounce troy = 1.097 ounces avoirdupois. 1 pound troy = 12 ounces troy; 1 pound avoirdupois = 14.58 ounces troy. 1000 ounces troy = 31.15 kg = 0.03115 tonnes.

SPECIAL UNITS IN THE CHEMICAL INDUSTRY

PETROLEUM AND REFINERY PRODUCTS

Crude oil and some refinery products are traded in barrels (bbl) of 42 US gallons (gal) (= 35 Imperial gal). As the gallon is a unit of volume, the weight of a barrel depends on the density of the product. Approximate conversion factors follow:

1000 lb = 3.32 bbl crude oil, 3.83 bbl gasoline, 3.54 bbl kerosene, 3.40 bbl gas oil, and 3.04 bbl fuel oil.
1 tonne = 7.33 bbl crude oil, 8.45 bbl gasoline, 7.80 bbl kerosene, 7.50 bbl gas oil, and 6.70 bbl fuel oil.

Liquefied petroleum gases are sold by the US gallon or by the tonne. One tonne contains 521 gallons of propane, 453 gallons of *n*-butane or 469 gallons of isobutane. LPG can be mainly propane, mainly butane, or a "mixed" cargo, in which case intermediate conversion factors based on composition must be applied.

GASES

Natural gas is measured in standard cubic feet (scf) at 1 atmosphere (atm) and 60°F or in cubic meters (m^3) at 1 atm and 0°C. 1 m^3 = 37.33 scf; 1 scf = 0.0268 m^3. Thermal units (heat liberated when a volume of gas is burned) are sometimes used. Calorific values depend on the composition of the gas but are usually 900–1000 Btu scf^{-1}. Accordingly 1 therm = 10^5 Btu = 100–110 scf.

Other gases are also measured in scf and m^3. If the molecular weight of a gas is M, then 10^6 scf of the gas weigh 2.635 M thousand pounds. For example, 10^6 scf of hydrogen weigh 5.312 thousand pounds and of oxygen 84.32 thousand pounds. Similarly, 1000 m^3 of a gas weigh 0.0446 M tonnes. 1000 m^3 of hydrogen weigh 0.0900 tonnes and of oxygen 1.427 tonnes.

COAL TAR PRODUCTS

Coal tar and materials traditionally derived from it such as benzene, toluene, and xylenes are sometimes measured in thousands of US gallons. One thousand US gallons of benzene at 20°C weigh 7320 lb, of toluene 7210 lb, of *o*-xylene 7300 lb, of *m*-xylene 7161 lb, and of *p*-xylene 7134 lb.

ETHANOL

Ethanol is measured in mixed volume and concentration units. One Imperial gallon (1.201 US gal) of 100% ethanol contains the same amount of ethanol as 1.75 proof gal, and concentration is measured in degrees proof. The specific gravity of ethanol is 0.79, hence 1 proof gal contains 4.5 lb (2.04 kg) ethanol. It is also the alcoholic equivalent of a US liquid gal at 15°C containing 50% ethanol by volume. The metric units are hectoliters (= 100 liters), and concentration is expressed in degrees Gay-Lussac. Ninety-five degrees Gay-Lussac represents 95% by volume at 15°C. One hectoliter = 22 Imperial gal = 26.4 US gal. One hectoliter of 100% ethanol weighs 174 lb (79 kg). The US liquid gallon (as above) is identical with the Queen Anne wine gallon. A US tax gallon for spirits of 100 proof or over is equivalent to the proof gallon; for spirits of less than 100 proof to the wine gallon.

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