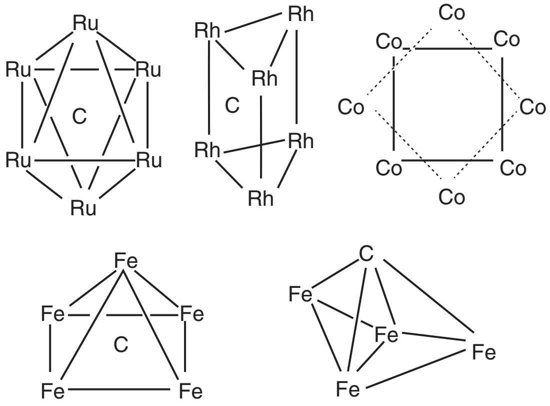
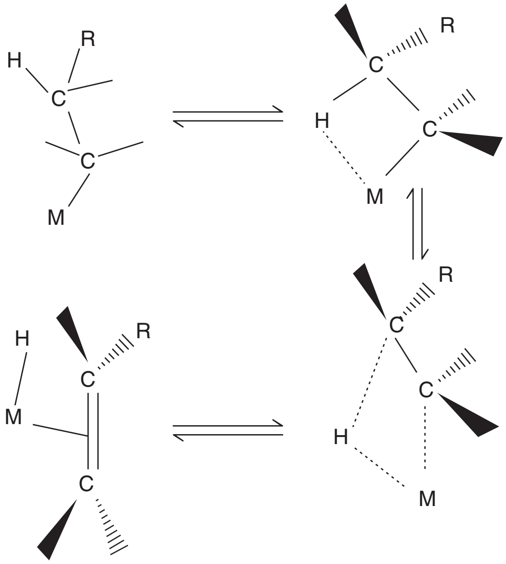


Figure 1.24 Nonreactive 'cage' and peripheral carbide clusters.



Scheme 1.21

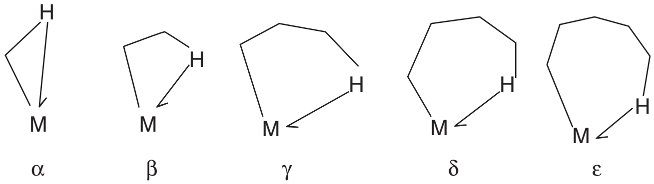
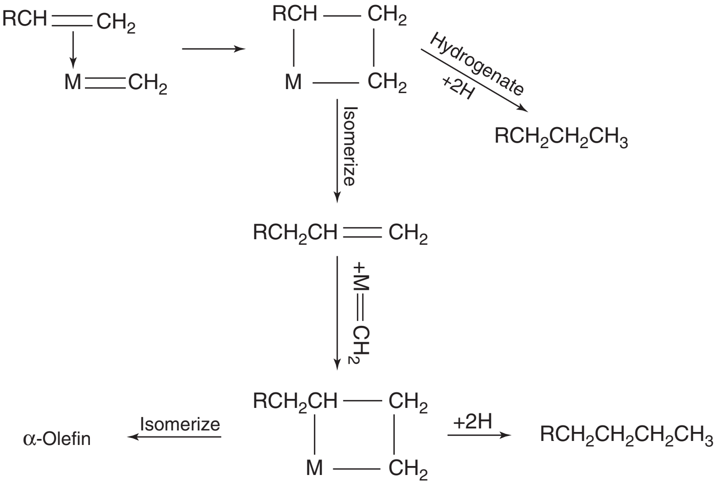


Figure 1.25 C–H environments for agostic interactions in organometallic complexes.



Scheme 1.22

1.5
Key Advances in Recent Theoretical Treatments: Universability in Heterogeneous Catalysis

In their conceptual and computational approach to *Molecular Heterogeneous Catalysis,* van Santen and Neurock (2006) have dealt with the essential ingredients to appreciate the complexity and status of catalysis from the viewpoints of the theoretical chemist and physicist – see also Norskov *et al.* (2002). It will be seen that the Brønsted–Evans-Polanyi (BEP) relation, which is rapidly gaining prominence in interpretations of catalytic phenomena, is of major importance. Based on an extensive set of DFT calculations (see Sections 5.7 and 5.8), Norskov *et al.* showed that, for a certain class of catalytic reaction, there is a universal reactant independent relation between the reaction activation energy and the stability of reaction intermediates. This leads directly to a universal relationship between absorption energies and catalytic activity, which can be used to pinpoint what it is that determines the best catalyst for a given reaction. In Chapter 2 we shall elaborate this approach further. Suffice it to say that, thanks to DFT in the hands of Nørskov and his school, we can explain why the following facts hold good:

- Ru and Fe are the best catalysts for ammonia synthesis,
- Co, Ru and Fe are the best catalysts for the Fischer–Tropsch synthesis,
- Pt, Pd and Ag are the best oxidation catalysts,
- Pd, Pt and Rh are the best auto-exhaust catalysts for removal of nitric oxide.

Elucidating the crystal structure of a heterogeneous catalyst is of prime importance on the road to understanding the mechanism of its action and also in suggesting related new structures worthy of synthesis. When it is difficult or impossible to obtain single crystals, or well-ordered, phase pure-powdered specimens of a given catalyst, much progress can be made via *atomistic simulations.* Considerable progress has been made in the development of interatomic potential that can be utilized to carry out *energy minimizations* in order to find the most stable structures for different oxide metal and zeolite systems. The reader is again referred to the monograph by van Santen and Neurock (2006) and also to one edited by Catlow (1997). Lattice energy minimization techniques have been quite successful in simulating the lowest energy structures of various metal oxides, zeolites and microporous aluminophosphates (ALPOS).

The programme known as GULP (General Utility Lattice Programme) developed by Gale is a general method towards simulating the structure and energetic for 3D ionic and molecular solids as 'defect' structures. It allows the calculation of a range of structural, mechanical and thermodynamic properties including relative energies, the preferred sitings of sorbates, bulk modulus, Young's modulus, dielectric constant refractive index, phonon and other vibrational frequencies, entropy, heat capacity and Helmholtz free energy.

1.5.1
Some Major Current Developments in Heterogeneous Catalysis

Particle-size effects constitute one of the major topics of investigation at present, especially in regard to the remarkable catalytic performance of gold nanoparticles. Bimetallic nanoparticles, which are already extensively used in catalytic reforming in the petroleum industry ever since pioneering work of Sinfelt, have undergone a renaissance, largely because smaller (and frequently mono disperse) nanoparticles exhibiting high activity and selectivity may now be routinely prepared from molecular precursors. Also because of improvements in preparative techniques, the complex phenomena of fluctuations and bistabilities on catalyst nanoparticles has become highly prominent. This, in turn, has demanded a re-examination of the role of catalyst support as a determinant of activity and selectivity.

A significant and growing area in heterogeneous catalysis is the design and exceptional performance of single-site catalysts, which exhibit many of the advantages of molecular (homogeneous) catalysts and metalloenzymes, but few of their disadvantages in that separation of products from reactants is readily effected. Apart from initiating a new era – in asymmetric heterogeneous catalysis and a return to the prospects of exploiting chiral surfaces in electrocatalytic and related fields – single-site catalysts offer one of the very few widely applicable strategies for the design of new catalysts (see Section 9.8).

Other major topics of great interest are:

- the design and preparation of solid-acid catalysts, a topic of continuing interest to one of us (see Thomas (1992));
- the catalytic breakdown of biomass;
- the functionalization of abundant naturally occurring hydrocarbons;

- (as outlined earlier in this chapter) the conversion of highly functionalized organic species in the plant world into feedstocks and fuels of the kind summarized in Figure 1.4.

All these topics will be considered in greater detail in later chapters, especially Sections 9.6 and 9.7.

1.6
Milestones Reached in Industrial Catalysis in the Twentieth Century, and Some Consequential Challenges

The milestones reached (Table 1.3) in catalysis in industrial challenges in the twentieth century signifies the central importance of the subject in the creation of wealth. But the general public is rightly becoming more concerned with environmental issues, and decisions are now being made that are not primarily based on science and technology. Public concern is a potent influence; and for many industries where catalysis already looms large it is becoming increasingly difficult to obtain permits, eliminate waste, construct incinerators and receive and transport toxic or otherwise hazardous materials.

In the twenty-first century it will become increasingly necessary to devise processes with close to 100% yields, to effect catalyst recovery, to regenerate and to recycle on a routine basis, and in all this catalysis will play an increasingly dominant role. Elimination of by-products and process waste is becoming a major issue and will demonstrably determine the viability of future chemical processes. It is a sign of the times that the State of California decreed that, in AD 2000, 2% of the motor vehicles on its roads must have zero deleterious emission, even though ways of securing this end at the time of the edict were by no means clear.

Hazardous and toxic materials such as HF, HCN, HCl, H_2SO_4, H_3PO_4, CI_2, acrylonitrile, formaldehyde, ethylene oxide and phosgene, for example are more-or-less essential building reagents in the chemical industry since they often possess reactivity or functionality required for further chemical reactions. Future business practices which entail the inventory and transportation of these materials will almost certainly have to be avoided or drastically diminished.

Methyl isocyanate (MIC) is familiar as it was at the centre of the tragic incident that occurred in Bhopal, India, some years ago. At that time and in that place MIC was produced by the phosgenation of methylamine:

$$CH_3NH_2 + COCI_2 \rightarrow CH_3NCO + 2\,HC1$$

It is no longer acceptable to store MIC as was done in Bhopal, and the use of reagents such as phosgene is greatly discouraged. The consequence of this is that industrial companies have sought, and succeeded in producing, safer alternatives. The DuPont Company, for example now use the catalytic dehydrogenation process (although by 1993 they had not yet disclosed the nature of the catalysts that they

Table 1.3 Milestones in the introduction of industrial heterogeneous catalysis during the twentieth century.

Decade	Process	Catalyst (prime constituent)
1900	Methane from $CO + H_2$ (syn-gas)	Ni
	Hydrogenation of fat	Ni
1910	Liquefaction of coal	Fe
	Synthesis of ammonia from $N_2 + H_2$	Fe/K
	Oxidation of ammonia to nitric acid	Pt
1920	High-pressure synthesis of methanol from $CO + H_2$	(Zn, Cr) oxide
	Fischer–Tropsch synthesis of alkanes, alkenes and alkanols from $CO + H_2$	Co, Fe
	Oxidation of SO_2 to SO_3 (sulfuric acid production)	V_2O_5
1930	Catalytic cracking of oil (fixed-bed, Houdry process)	Montmorillonite clays
	Epoxidation of ethylene	Ag
	Oxidation of benzene to maleic anhydride	V
1940	Catalytic reforming of hydrocarbons (gasoline)	Pt/Al_2O_3
	Hydrogenation of benzene to cyclohexane	Ni, Pt
	Inversion of sucrose (and decolourization of golden syrup)	Immobilized enzyme (invertase) on charcoal
1950	Polymerization of ethylene to polyethylene:	
	Ziegler–Natta	Ti
	Phillips process	Cr
	Production of polypropylene and polybutadiene (Ziegler–Natta)	Ti
	Hydrodesulfurization	(Co, Mo) sulfides
	Hydrotreatment of naphtha	$Co–Mo/Al_2O_3$
	Oxidation of naphthalene to phthalic anhydride	(V, Mo) oxides
1960	Oxidation of butane to maleic anhydride in O_2	$(VO)_2P_2O_7$
	Oxidation of propylene to acrolein	(Bi, Mo) oxides
	Ammoxidation of propylene to acrylonitrile	(Bi, Mo) oxides
	Improved means of reforming hydrocarbons	Pt–Ir on $A1_2O_3$ Pt–Re on $A1_2O_{3vz}$
	Metathesis of alkenes	(W, Mo or Re) oxides
	Improved means of cracking of hydrocarbons	Zeolites (Faujasite-based)
	Production of vinyl acetate from ethylene	Pd/Cu
		Cu chloride
	Oxychlorination of ethylene to vinyl chloride	
	Triolefin process (propylene to butene and ethylene)	$Mo(CO)_6$ or $W(CO)_6$ on $A1_2O_3$
	Production of *ortho-xylene* from phthalic anhydride	V_2O_5 on TiO_2
	Hydrocracking	$Ni–W/Al_2O_3$
	Water-gas shift (at high temperatures)	$Fe_2O_3/Cr_2O_3/MgO$
	Water-gas shift (at low temperatures)	$CuO/ZnO/Al_2O_3$

(*continued overleaf*)

Table 1.3 (*Continued*)

Decade	Process	Catalyst (prime constituent)
1970	Xylene isomerization (shape-selective formation of *para*-xylene)	H-ZSM-5 (zeolite)
	Methanol from $CO + H_2$	$Cu-Zn/Al_2O_3$
	Disproportionation of toluene to benzene and *para*-xylene	H-ZSM-5
	Catalytic dewaxing	H-ZSM-5
	Auto-exhaust catalyst	Pt, Rh, Pd on oxide
	Conversion of benzylpenicillin into 6-aminopenicillanic acid (production of semisynthetic penicillins)	Immobilized enzyme (penicillin amidase)
	Isomerization of glucose to fructose	Immobilized glucose isomerase
	Hydroisomerization	Pt/zeolite
	Selective reduction of NO with NH_3	V_2O_5 on TiO_2
	Production of MTBE (methyl *t*-butyl ether) from methanol and 2-methylpropylene	Acidic ion-exchange resins
	Fructose-enriched from glucose (from glucose syrup)	Immobilized cells (*Arthrobacter*)
	Hydrolysis of raffinose	Immobilized cells (*Mortierella vinacea*)
1980	Conversion of ethylene and benzene into ethylbenzene	H-ZSM-5
	Methanol to gasoline (petrol) (MTG)	H-ZSM-5
	Conversion of ethylene and acetic acid into vinyl acetate	Pd
	Oxidation of *t*-butanol to methyl methacrylate	Mo oxides
	Improved means of liquefying coal	(Co, Ni) sulfides
	Production of diesel fuel from $CO + H_2$ (syn-gas)	Co
	Hydrotreatment of hydrocarbons	Pt/zeolite Ni/zeolite H^+-Ferrierite
	Catalytic distillation (in MTBE production)	Acidic ion-exchange resins
	Vitamin K_4 production	Pd membrane
	Dehydrocyclization (‘Cyclar’) of alkanes	Ga–ZSM5
	Conversion of light alkanes to aromatics	
	Oxidation of methacrolein	Mo–V–P (hetero-polyacid)
	Hydration of isobutene	
	Polymerization of tetrahydrofuran	Phase-transfer catalysis
1990	Production of dimethyl carbonate from acetone	Cu chloride
	Conversion of phenol to hydroquinone and catechol	Ti–silicalite
	Isomerization of but-l-ene to 2-methylpropylene	H^+-Ferrierite acidic H^+-Theta-1 zeolites

Table 1.3 (*Continued*)

Decade	Process	Catalyst (prime constituent)
	Isomerization of oxime of cyclohexanone to ϵ-caprolactam	Silicoalumino-phosphate molecular sieve (SAPO-11)
	Ammoxidation of cyclohexanone to its oxime using H_2O_2	Ti–silicalite
1990	Production of acrylamide from vinyl cyanide	Immobilized nitrile hydratase
	Complete combustion of natural gas (at about 1300 °C)	Noble metals and/or mixed oxides
	'Sweetening' of natural gas by selective oxidation of H_2S to S	Mixed oxides
	Oxidation of benzene to phenol via cyclohexene	Zeolite
	Methanol to light alkenes	Silicoalumino-phosphate molecular sieve (SAPO-34)
	Olefin oligomerization (Shell polygasoline and kerosene process)	Zeolite
	Production of L-aspartic acid and L-alanine from ammonium fumarate	Immobilized micro-organisms
	Conversion of toluene into toluene *cis*-glycol	*Pseudomonas putida*
	Production of 2,6-diisopropylnaphthalene using propylene as alkylating agent	Acidic zeolite (mordenite)
	Decomposition of hypochlorite	NiO
	Dehydration of alkanols	Heteropolyacid salts

developed for these reactions):

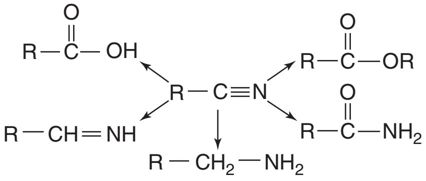
$$CH_3NH_2 \xrightarrow{CO} CH_3NHCHO \xrightarrow{O_2} CH_3NCO$$

The DuPont strategy enables them to make MIC and to convert it *in situ* into an important agrichemical product. *In situ* manufacture will become progressively more prominent in the twenty-first century, since it greatly reduces the risk of unwanted exposure.

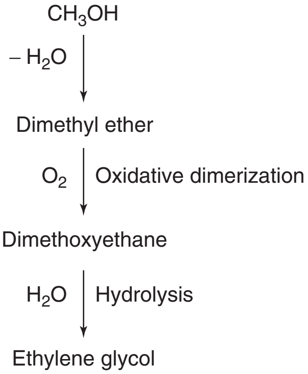
This example, entailing a re-analysis of the entire mode of manufacture, could be replaced many times over. The EniChem Company in Italy, in its novel catalytic method of manufacturing the useful monomer dimethyl carbonate, which formerly used massive quantities of phosgene, now follows the following 'safe' process:

$$CH_3COCH_3 + O_2 \rightarrow (CH_3)_2CO_3$$

Yet another example concerns hydrogen cyanide (prussic acid), HCN, which is the starting point for introducing the versatile nitrile functionality in a wide range of organic commodities. Amides, acids, amines, esters, and so on, are all readily generated from the corresponding nitrile (Scheme 1.23).



Scheme 1.23

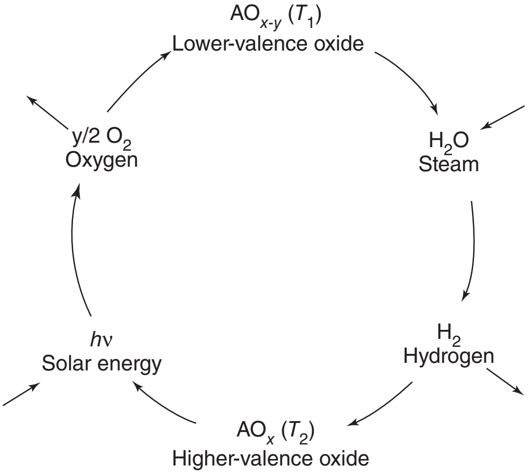


Scheme 1.24 Production of ethylene glycol from methanol.

All this underlies the recognition that catalysis is of central importance, and is likely to remain so into the foreseeable future, in securing environmentally benign products. Catalysis likewise holds the key to the safer and cheaper manufacture of desirable products. Typical processes are shown in Schemes 1.24 and 1.25.

An attractive method for the utilization of solar energy is its direct conversion into chemical fuels (e.g. syn-gas), thereby making it available as a source either of chemical feedstock, or of heat (by catalytically effecting a reverse reaction – see Figure 1.26), or both. The Russian ADAM–EVA cycle depicted in Figure 1.26 is already functioning smoothly. Recent advances in capturing solar energy are given in Chapter 8 and 9.

Conceptually it is convenient to divide the future challenges into broad categories such as environmental (Figure 1.27), technological (including biotechnological) (Figure 1.28) and fundamental. And although it is possible to draw up a list of targets as is done in these tables, it must never be forgotten that these three categories are quite arbitrary; the distinctions between them are blurred. Purists rightly argue that, in most circumstances, the solutions to practical problems almost invariably demand a deeper understanding of fundamentals. Moreover, distinctions between the technological and biotechnological can themselves be fuzzy. Recall that hitherto, for example the source of C_{10}–C_{14}-hydrocarbons for use in, say, detergency was petrochemical. Nowadays, thanks to major advances in the production of transgenic plants and other consequences of the molecular biological revolution, it is possible to develop oilseed rape hybrids rich in C_{12}-oils. Other routes are described in Sections 9.6 and 9.7. And when it



Scheme 1.25 Thermochemical cycles with metal oxide for the production of hydrogen from water. Ideally the higher' oxide needs to decompose (catalytically) very rapidly at a high temperature T_2 and the steam to react with the 'lower' oxide at a low temperature T_1.

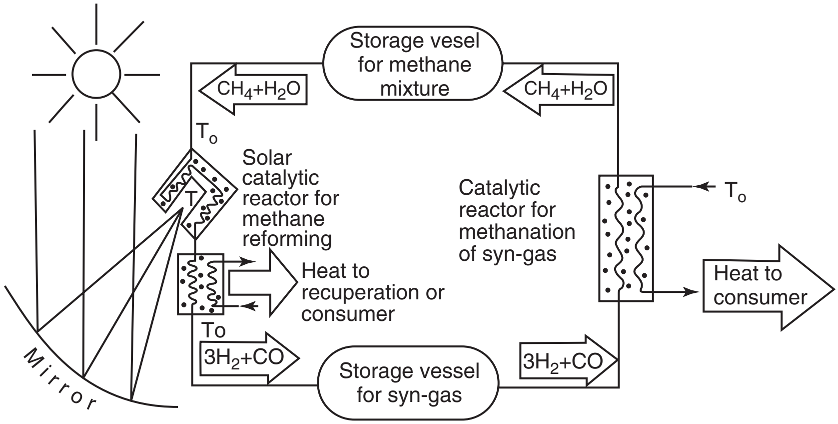


Figure 1.26 Scheme of thermocatalytic conversion of solar energy based on the closed thermochemical 'ADAM–EVA' cycle; T is the temperature inside the cavity of the solar catalytic reactor; T_o is the temperature of environment. With permission from Zamaraev (1996).

comes to biocatalysts, and the use of immobilized cells, modified organisms or cloned genes (to generate spectacularly stereoselective and active catalysts), the distinction between heterogeneous and homogeneous systems also becomes less well defined.

Returning to fundamentals, it is almost a truism that the perennial quest has to be understanding the factors that enhance specificity, increase activity and improve lifetime. A better catalyst must, by definition, do one or all of these things. To understand better how we may achieve these ends is the pervasive theme of this book.

- Development of ‘zero-waste’ processes
- Minimization of hazardous products and ‘greenhouse’ gases
- Replacement of corrosive liquid acid catalysts by benign solid acid catalysts
- Evolution of sustainable systems
- Reduction in volume of by-products (avoidance of processes that generate salts)
- Development of processes requiring less ‘consumption’ of catalysts
- Elimination of voluminous by-products

Figure 1.27 Selection of environmental challenges.

Challenge

- Reformulated transport fuels (containing lower amounts of aromatics and volatile components, and larger amounts of more completely combustible additives)
- Development of (catalytic) automobiles operating on methanol dissociation[i]
- Better catalysts for hydrodesulfurization, hydrodenitrification of light oils and coals and hydro-treatment of heavy oils and tars
- Single-step synthesis of desirable products:
    - — acetaldehyde from ethane
    - — aromatics from ethane
    - — phenol from benzene
    - — acrolein from propane
    - — acrylonitrile from propane by ammoxidation[ii]
    - — acetic acid from methanol
    - — 2-methylpropylene from syn-gas
- Better methods for isomerizing linear alkanes into branched-chain ones
- Functionalization of light alkanes, especially methane (e.g. by use of heterogenized metalloporphyrins, P450s or cytochromes)
- Efficient routes to cheaper feedstocks for the chemical and pharmaceutical industries[iii]
- Development of robust, re-usable, chiral catalysts
- New shape-selective catalysts, for example, for non-thermodynamic ratios of mono- and di-methylamines from methanol and ammonia
- Development of processes using CO_2 as reactant[iv]
- Cheaper and safer methods of generating hydrogen[v]
- New catalytic membranes[vi]
- Better electrocatalysts for fuel-cell consumption of plentiful hydrocarbons
- Development of modified enzymes, organisms or transgenic plants for ‘natural’ production of polymers[vii]
- Families of solid catalysts for ‘tunable’ conversion of methanol into either ethylene or propylene
- Fischer–Tropsch catalysts for sharply defined reaction products
- Efficient, safe methods of generating hydrogen peroxide (from H_2 and O_2)[viii]
- Designed solids capable of controlled release of structural elements such as oxygen or hydrogen
- Uniform, molecular-sieve catalysts (of redox or Brønsted type) possessing well-defined larger pores (40–100 Å diameter)
- Engineered proteins for pharmaceutical use[ix]

Figure 1.28 Selection of technological challenges.

i A vehicle running on a fuel in which methanol dissociates to CO and H_2 on board has many attractions. First, such a fuel is more efficient than undissociated methanol. Second, the heat required for endothermic dissociation of the alcohol can be supplied by the engine exhaust gas. This recovers waste heat and increases the heating value of the fuel. Third, an engine functioning in this manner can be operated with excess air (*i.e.*, under lean burning conditions), which facilitates the complete combustion of CO and hydrocarbons. Lastly, problems associated with formaldehyde emission are appreciably reduced, and emissions of the oxides of nitrogen are likewise greatly diminished.

ii Section 9.5.2

iii Sections 9.6 and 9.7

iv Section 9.5.4.1

v Section 9.4

vi Section 8.5.2

vii Section 9.6

Zeneca plc (formerly ICI) produced 100 tons of the natural polymer Biopol in 1993. Biopol is a bacterial storage polymer, produced by fermentation of an alkaligenous strain. It consists of polyhydroxybutyrate or a copolymer with polyhydroxyvalerate. It is both biocompatible and biodegradable

viii In 1992, several companies including Mitsubishi, DuPont and Interox announced palladium-or platinum-based catalysts for this synthesis.

ix Section 9.6

Figure 1.28 (*Continued*)

Problems

These problems focus largely on thermodynamic and a little on strategic aspects of catalysis. They are intended to consolidate the readers assumed acquaintance with thermodynamic and related considerations. In each subsequent chapter the problems set are linked directly to the topics discussed in that chapter, and serve to illustrate or extend the relevant principles.

1.1 Using only thermodynamic principles, show that for any given temperature and total pressure the maximum conversion of hydrogen into ammonia occurs when the ratio of hydrogen to nitrogen in the feed gas to an ammonia synthesis reactor is 3 : 1.

1.2 Natural gas consists chiefly of methane. It has been suggested that one way of avoiding dependence on oil for the production of important chemicals is for benzene to be produced according to the following reaction:

$$6\ CH_4(g) \rightarrow C_6H_6(g) + 9\ H_2(g)$$

Before embarking on a search for a suitable catalyst to effect this conversion, we must first determine whether this reaction is feasible. Pursue this question quantitatively given that ΔC_P for the above reaction is:

$$\begin{aligned} &42.0 - 32.1 \times 10^{-3}T + 3.83 \times 10^{-6}T^2 \text{cal K}^{-1}\text{mol}^{-1} \\ &\quad = 176 - 134 \times 10^{-3}T + 16.0 \times 10^{-6}T^2\ \text{J K}^{-1}\text{mol}^{-1} \end{aligned}$$

(Hint: You should begin by consulting thermodynamic tables in other text books, or in National Bureau of Standards compilations, and work out $\Delta H^{\ominus}_{298}$ and $\Delta S^{\ominus}_{298}$ for the proposed reaction.)

1.3 Investigate the effect of temperature on the disproportionation of toluene, given the accompanying data.

T (°C)	50	100	150	200	250
K_o	0.059	0.065	0.070	0.074	0.078
K_m	0.206	0.208	0.209	0.210	0.211
K_p	0.0837	0.0875	0.0904	0.0928	0.0949

K_o, K_m, K_p are thermodynamic equilibrium constants for the disproportionation reaction yielding benzene and *ortho-*, *meta-* or *para*-xylene respectively.

What temperature would you choose to effect (a) the best conversion into *m*-xylene and (b) the best conversion to benzene? What effect would total pressure have on the product distribution?

1.4 Choose an approximate operating pressure for the industrial preparation at 500 °C of methanol from synthesis gas (a mixture of carbon monoxide and hydrogen), given the following data on free energies ($\Delta G^\ominus$) and enthalpies ($\Delta H^\ominus$) of formation:

	CO(g)	CH_3OH(g)
$\Delta G^\ominus_{298}$ (kJ mol^{-1})	−7 836	−9 241
$\Delta H^\ominus_{298}$ (kJ mol^{-1})	−6 310	−11 483

1.5 The composition of a gas emerging from the secondary reformer of a modern ammonia plant has the following composition:

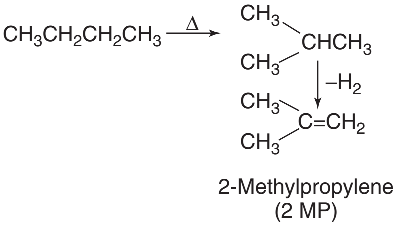
39.5% H_2, 16.3% N_2, 28.3% H_2O, 4.5% CO_2, 10.7% CO, 0.2% A and 0.5% CH_4

Assuming that equilibrium is established, what would the CO content of this gas be if it were fed directly to the first stage of a shift converter employing an iron oxide/chromium oxide catalyst and operating at 450 °C? The equilibrium constant for the reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

is 7.337 at 450 °C. Why is it normal practice to have a low-temperature (about 250 °C) shift converter as a second stage? Would the same catalyst as used for the high-temperature (first) stage be an appropriate choice for the second stage?

1.6 With the phase-down in the use of lead additives in petrol (gasoline), there is a growing need to obtain blending agents which have high octane numbers. One such material is methyl *tert-butyl* ether, MTBE (2-methyl-2-methoxypropane). It can be synthesized, using clay catalysts (see Ballantine *et al.* (1985)) from isobutene (2-methylpropylene (2MP)). An attractive route for the production of isobutene, which is comparatively scarce in contrast to methanol, of which there is a glut, is to take *n*-butane (from natural gas), isomerize it to isobutane (iB) and then to dehydrogenate the latter to 2-methylpropylene (2MP), as shown in Scheme 1.26. Shape-selective zeolitic catalysts are good for the first and platinum on



Scheme 1.26 Production of 2-methylpropene from *n*-butane.

alumina for the second of these two steps. Of considerable importance in designing a feasible operating system are the equilibrium fractions of the various possible isomers. These equilibrium fractions are shown in Figure 1.29 for a total pressure of 1 bar.

Explain how such quantitative information is derived; and discuss which temperature ranges are the most appropriate for overall conversion. Consult the literature (e.g. Natarajan, Wright and Thomas (1993)) for an alternative catalytic route to 2MP.

1.7 A popular method of producing formaldehyde on an industrial scale is to pass a mixture of methanol vapour and air at a total pressure of 1 bar over a metallic silver catalyst at 550 °C. During the course of this process, the silver slowly loses its lustre and gradually disintegrates. Using the following data, examine whether this might be due to the formation of silver oxide:

$$\Delta G^{\ominus}_{298}(\mathrm{Ag_2O}) = -10.826\ \mathrm{kJ\ mol^{-1}}$$
$$\Delta H^{\ominus}_{298}(\mathrm{Ag_2O}) = -30.556\ \mathrm{kJ\ mol^{-1}}$$

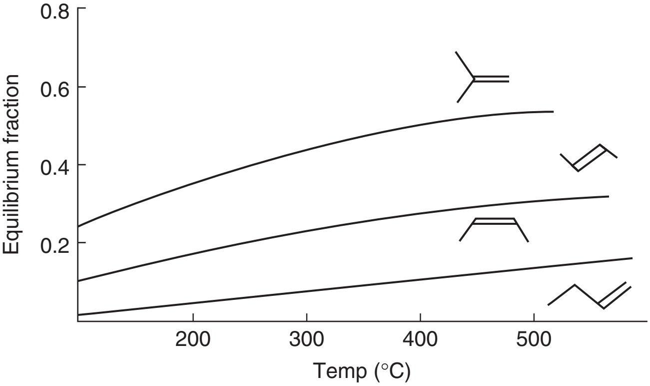
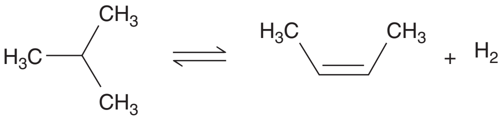


Figure 1.29 Equilibrium fraction of various alkenes in the thermal dehydrogenation of isobutane:



The relevant heat capacities (J K^{-1} mol^{-1}) are: Ag, 26.75; Ag_2O, 65.63 and O_2, 31.35.

1.8 Benzaldehyde can be generated from carbon monoxide and benzene over an appropriate catalyst at 50 °C and 500 bar total pressure. Given the information below, describe the calculations by which you would estimate an upper limit to the fraction of the benzene converted into benzaldehyde:

a) heat capacities and standard free energies and enthalpies of the compounds in question at 298 K;
b) the densities of benzene and benzaldehyde at 298 K;
c) $p-V$ data for carbon monoxide at 20 and 30 °C in the pressure range up to 500 bar.

1.9 Nitric oxide leads to the depletion of the ozone layer ($NO + O_3 \rightarrow NO_2 + O_2$). Since NO is liberated in vast quantities from power stations currently in use, efforts are now underway to reduce its concentration by catalytic ammoxidation using $V_2O_5-TiO_2$. One such reaction is: $4\ NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$. Write down other feasible reactions leading to N_2 or N_2O and H_2O as sole products. From thermodynamic data, estimate the equilibrium constants of these reactions.

1.10 Several strategies are available for the use of catalysts in harnessing solar energy. One of these, illustrated in Figure 1.26, is the so-called ADAM–EVA cycle operated by the Boreskov Institute; another, by the Weizmann Institute in Israel, has been described (Dostrovsky, 1991). Both these thermocatalytic converters entail the cycle of 'syn-gas' production (from the endothermic reaction $CH_4 + H_2O$) followed by methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$) with liberation of heat. But several other strategies are available, for example production of syn-gas and production of hydrogen.

a) Indicating which catalyst and the reactor conditions you would use, draw up a minimum of eight specific syntheses of products (such as alkanes, alkenes, alkanols and gasoline) that could be produced from a solar furnace.
b) Starting from either Fe_2O_3 or Fe_3O_4 and water, describe a feasible set of reactions and conditions (including appropriate catalysts) for the solar production of hydrogen and oxygen.

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