Excursions into multiphase reactions*

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Abstract. Multiphase reactions are ubiquitous in the chemical industry and a rational analysis of reactors where they are conducted requires an intimate knowledge of chemical kinetics, thermodynamics, mass transfer and fluid mechanics. In many situations in practice, conducting reactions in multiphase systems is advantageous as compared to that in a single liquid phase system.

The use of phase transfer catalysts, micellar catalysts, emulsifiers, hydrotropic agents etc., can significantly enhance the rates of multiphase reactions. A change-over from gas-liquid to liquid-liquid mode of operation could also have favourable influence. Solid-liquid reactions have received limited attention and many aspects need to be studied intensively. Three-phase reactions offer some fascinating features. The effect of solid particles, which may be sparingly soluble reactant, catalyst or even alien material, can be very substantial.

Multiphase biochemical and electrochemical reactions have many unique features and such reactions are becoming increasingly important. Novel strategies of conducting multiphase reactions have been developed of late, though there are plenty of problems yet to be tackled.

Keywords. Multiphase reactions; chemical industry; chemical kinetics; thermodynamics; mass transfer; fluid mechanics.

1. Introduction

Multiphase reactions are crucial in the chemical industry and encompass a wide variety of systems. An understanding of these reactions, and the reactors where they are conducted, constitutes the foundation stone of modern chemical engineering. The analysis and design of multiphase reactors place chemical engineers in a commanding position to be able to interconnect chemical kinetics, thermodynamics, mass transfer and fluid mechanics. In addition, the question of the dynamics of these reactors, including problems of stability, can be tackled.

This subject has acquired some maturity but the sheer complexity, associated with a wide variety of gas-liquid, liquid-liquid, gas-liquid-solid, multiphase electrochemical and biochemical reactions, offers a large number of problems yet to be satisfactorily solved. An attempt will be made to first present, albeit succinctly, some problems which have been studied and which bring out some unique features. In this presentation, attention will be focussed only on those multiphase reactions where at least one liquid phase is encountered.

It would be pertinent to emphasise that a large number of industrially important reactions involve solid-catalysed vapour phase systems. It may look superficially attractive, at least in some systems, to change-over from solid-catalysed vapour phase reactions to, say, melt-catalysed gas-liquid or liquid-liquid reactions, so that the heat load can be conveniently handled and catalyst poisoning can be successfully overcome.

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This apparent simplicity is somewhat deceptive as it is hedged by the fact that effective interfacial areas in fluid-fluid systems are trivial fractions of those available through porous solid-catalysed reactions. Gas-liquid reactions would generally offer interfacial areas less than $10\text{ cm}^2/\text{cm}^3$ of melt. By contrast, in solid-catalysed vapour phase reactions, we may have values in the range of 10^5 to 10^6 (or even 5×10^6) cm^2/cm^3 .

Multiphase reactions are relevant in practice not only by virtue of being an integral part of processes but also by way of deliberate imposition to achieve certain definite results associated with the degree of removal of a solute gas, speeding-up rates of physical absorption/extraction, recovery of chemicals from waste streams etc. Further in many cases of practical relevance we convert homogeneous reaction systems to two-phase systems to achieve certain objectives such as use of cheaper reactants, ease of removal of product, cheaper and more convenient process-operating conditions, higher selectivity with respect to the desired product etc.

The use of phase transfer catalysts, micellar catalysts, emulsifiers, hydrotropic agents etc can cause considerable enhancements in heterogeneous reaction rates. The presence of solid particles finer than the diffusion film thickness can also have significant effects on the rates in three-phase slurry reactors.

Biochemical and electrochemical reactions in multiphase reactions have also generated a lot of interest.

Some novel aspects of gas-liquid and liquid-liquid reactions have been considered recently (Sharma 1983, 1984). A recent book by Doraiswamy & Sharma (1984) is a comprehensive treatise on analysis, examples and design of heterogeneous systems.

2. Fast reactions in multiphase systems

Excursions into the domain of fast reactions where the half-life is well below 10^{-2} s are very common. Indeed the reactions of O_2 , CO, NO, CO_2 etc. with haemoglobin in human physiology provide classical examples as a backdrop for chemical industry. It is not uncommon for us to deal with reactions having half-lives even below a millionth of a second. It might appear somewhat infructuous to an uninitiated person as to why we should probe so much into the kinetics of such fast reactions. The main reason why we are so interested is that many systems in practice involve sparingly soluble solutes and thus, even for the type of fast reactions enumerated above, the throughput of the reactors is low. Thus we are constantly concerned with ways and means of studying fast reactions and of making them even faster.

As mentioned previously, in all heterogeneous reacting systems there is an interaction of kinetic and mass transfer factors. Depending on the relative rates of reaction and mass transfer it is possible to have different reaction regimes (Doraiswamy & Sharma 1984). In all mass transfer-dependent rates of heterogeneous reactions, the rate per unit volume of reactor will depend on the interfacial area. It is then more convenient to separate the effects of interfacial area and the factors that effect the rate per unit interfacial area—usually referred to as the specific rate of mass transfer (R_A).

2.1 Kinetics of fast reactions

We can study kinetics of exceedingly fast reactions in delightfully simple pieces of apparatus like a laminar jet or a stirred contactor with a flat interface. A number of investigations have been reported in the literature for gas-liquid, liquid-liquid and solid-liquid systems where first order or pseudo-first order reactions having rate

constants higher than 10^6 s^{-1} have been studied (Doraiswamy & Sharma 1984). The above study of kinetics requires by way of prerequisite that mass transfer is accompanied by fast pseudo-first order reaction in the immediate vicinity of the interface and the following equation holds (Doraiswamy & Sharma 1984):

$$R_A = [A^*] \{ (2/\overline{m} + 1) D_A k_{mn} [A^*]^{m-1} [B_0]^n \}^{1/2}$$

provided

$$\{ (2/\overline{m} + 1) D_A k_{mn} [A^*]^{m-1} [B_0]^n \}^{1/2} / k_L > 3 \\ \ll \{ [B_0] / Z [A^*] \} (D_B / D_A)^{1/2}$$

If the reaction between the dissolved solute and the dissolved reactive species is instantaneous and hence is mass-transfer limited then we have a methodology of obtaining diffusivity of dissolved reactive species as the following equation holds (Doraiswamy & Sharma 1984):

$$R_A \simeq k_L \{ [B_0] / Z \} (D_B / D_A)^{1/2}$$

provided

$$\{ (2/\overline{m} + 1) D_A k_{mn} [A^*]^{m-1} [B_0]^n \}^{1/2} / k_L \gg \{ [B_0] / Z [A^*] \} (D_B / D_A)^{1/2} \gg 3$$

Measurements of D_B have been made for amines and cuprous amine complexes (daSilva & Danckwerts 1968; Sridharan & Sharma 1976)

3. Strategies for increasing rates in heterogeneous reacting systems

3.1 Increasing the rate constant by changing reactive species

In many absorption and extraction systems, we deliberately impose chemical reaction in order to keep the concentration of the dissolved species in the extracting phase zero and hence maintain a high driving force throughout the process. Thus, for instance, the removal of CO_2/COS from gases containing $\text{N}_2 + \text{H}_2$; CH_4 etc. can be affected by using potash solutions or aqueous solutions of alkanolamines (Sharma 1965; Danckwerts & Sharma 1966). Here by manipulating the reactive species, rates may be increased. For instance, the values of the second order rate constant for the reaction between COS and diethanolamine (DEA) and methylaminoethanol (MAE) are 1.09×10^4 and $2.09 \times 10^5 \text{ cm}^3/\text{mol}$, respectively (Sharma 1965). These reactions can lie in the fast reaction regime where the specific rate is given by:

$$R_A = [A^*] (D_A k_2 [B_0])^{1/2}; \quad \begin{pmatrix} m = 1 \\ n = 1 \end{pmatrix}$$

As seen from the rate expression, the rate is proportional to the square root of the second order rate constant. Hence R_A will go up by a factor of 4.3 when we switch over from DEA to MAE under otherwise similar operating conditions.

Similar strategies would also hold for liquid-liquid and solid-liquid systems.

A different strategy for the above example of COS removal in a liquid-liquid system would be to enhance the rate of extraction of COS from liquefied C_3 fractions into aqueous NaOH in the presence of phase transfer catalysts (see below).

3.2 Phase transfer catalysts (PTC)

Many homogeneous reactions, which take several hours to give reasonable yields and require severe process conditions, can be made to give attractive yields at ambient

conditions by deliberately switching over to a heterogeneous system and employing phase transfer catalysts. As the name suggests, the PTC complexes with a reactive ion in one phase and transfers it in the form of a complex to the other phase (for which the complex has a high partition coefficient) where it can react with the other reactant. Phase transfer catalysts thus overcome solubility limitations of heterogeneous systems by bringing both reactants into one phase and allowing them to react.

Common phase transfer catalysts include quaternary ammonium compounds like cetyl trimethyl ammonium bromide, trioctyl methyl ammonium chloride, crown ethers and polyethylene glycols. A number of heterogeneous liquid-liquid and solid-liquid reactions have been shown to be amenable to PTC (Yadav 1975; Dehmlow & Dehmlow 1980). Recently Lele *et al* (1983a) have shown how even fast reactions, such as, alkaline hydrolysis of higher formate esters are enhanced as much as 250 times by employing PTC.

Krishnakumar & Sharma (1983) have successfully employed PTC in the manufacture of triaryl phosphates and also to overcome steric hindrance in the case of *o*-substituted phenolic materials. This reaction, otherwise, requires very severe conditions and gives poor yields.

Bhave & Sharma (1983) found that the rate of extraction of COS from *n*-heptane into an aqueous phase containing NaOH was 25 times higher than that in the absence of PTC.

A lot of interest has been focussed on immobilizing PTC on a solid matrix (triphasic catalysis) to facilitate its removal from the reaction mixture (Regen 1975, 1979).

Yadav & Sharma (1981) have considered the manufacture of benzyl esters where solid sodium acetate/benzoate is reacted with benzyl chloride in the presence of PTC. This is an example of PTC in solid-liquid systems. This is perhaps one of the earliest examples going back to the 1920s where PTC, although not known by that name till the 1970s, was used. However, for nearly six decades the standard catalyst has been triethylamine which *in situ* gets converted to benzyl triethylammonium chloride (BTEAC). Yadav & Sharma (1981) have shown that other catalysts can be used which are almost 25 times better than BTEAC.

The role of PTC in gas-liquid systems has been reported by Tundo *et al* (1983) who obtained good results for inter-conversions of halides with 10% tetrabutylphosphonium-bromide on alumina. In a typical case, CH_2Cl_2 and $\text{C}_2\text{H}_5\text{Br}$ were reacted and CH_2Br_2 and CH_2ClBr were obtained. Even more interesting is the reaction between gaseous methyl chloride and aqueous sodium nitrite to give nitromethane (Markofsky 1983). Neumann & Sasson (1983) have reported high selectivity for alkyl aryl ethers by the alkoxylation of halobenzenes using polyethylene glycols as PTC. Ido *et al* (1983) have studied the kinetics of oxidation of benzyl alcohol with solid PTC. Szeja (1982) reports that catalytic esterification of alcohols and monosaccharides with acid chlorides in the presence of tetraalkylammonium salts and NaOH gave good yields of esters. A variety of oxidation reactions, some hydroformylation reactions etc., involving gas-liquid systems, have recently been shown to be amenable to adoption of PTC with some useful results (Lee 1982; Januszkiewicz & Alper 1983; Fukuoka *et al* 1984).

3.3 Micellar catalysis

Micelles are aggregates of surfactants (containing hydrophilic and hydrophobic chains) in water. Because of their hydrocarbon-like interior, they are capable of solubilizing

large quantities of hydrophobic substances. Ionic reagents are taken up due to electrostatic interactions. Because of the looseness of the aggregate structure, water can penetrate the micellar interior and hence the solubilised reactant can come in contact with both ionic and nonionic reagents in the aqueous phase as a result of which rates of solubility limited heterogeneous reactions may be drastically enhanced.

A number of reactions such as hydrolysis of esters, cyanation, oximation etc. have been shown to be amenable to micellar catalysis (Fendler & Fendler 1975; Bunton 1979). Recently, Janakiraman & Sharma (1982) developed theoretical models for micellar enhancements in heterogeneous systems. Rates of oximation of cycloalkanones (cyclododecanone, 4-*t*-butyl cyclohexanone) were found to be enhanced by 2–70 times in the presence of sodium lauryl sulphate micelles in both solid-liquid and liquid-liquid systems (Janakiraman & Sharma 1985a). Alkaline hydrolysis rate of phenyl benzoate (solid-liquid system) was observed to increase by 2–14 times in the presence of cationic surfactants (Janakiraman 1984). Skrzewski & Cichacz (1984) have studied the two-phase oxidation of some aromatic compounds with cerium ammonium nitrate. Sodium lauryl sulphate was found to enhance the reaction whereas cationic and nonionic surfactants inhibit it.

One of the main reasons why micelles have not been exploited in industry is that most of the work on micellar systems published so far concentrates only on homogeneous systems, where problems of separation of micelles from reaction products exist. These limitations do not exist in the solid-liquid systems where the product comes out as a separate solid phase. Even in the liquid-liquid systems, if at all there are any problems of emulsification, these may be overcome by proper selection of the organic phase solvent.

Bolden *et al* (1983) have reported that the solubility of gases like ethane and propane increased by as much as 4 and 9 times, respectively, in aqueous solutions of various sodium alkylsulphates. It was observed that below the CMC value the solubility was similar to that in water but at surfactant concentrations above the CMC the solubility increased linearly with increasing surfactant concentration. Hoskins & King (1981) have shown that the addition of *n*-pentanol can further enhance solubilities.

Micellar catalysis may also be applicable to gas-liquid systems such as removal of COS from C₃/C₄ gaseous streams into an aqueous NaOH solution or selective absorption of butenes from C₄ streams in aqueous solutions of sulphuric acid of different concentrations.

The use of micelles in controlling photochemical reactions has been recently reviewed (Ramamurthy 1984). Here micelles are known to affect the yields, selectivity and the stereochemical structure of the product. The compartmentalization of reactants within micelles leads to protection of the excited singlet and triplet state of the molecules by suppressing bimolecular quenching processes. This brings about changes in the selectivity of unimolecular photochemical reactions. Depending on its hydrophobic and hydrophilic moieties, the location and orientation of the substrate in the micelle can vary and, hence, can affect the regiochemistry of the product.

3.4 Role of emulsifiers in liquid-liquid systems

The rates of liquid-liquid reactions can be increased by addition of emulsifiers which increase interfacial area and hence the rates of mass transfer. Care must be taken, however, to see that no phase separation problems are encountered due to emulsification of the phases. Lele *et al* (1983b) have shown how the use of 0.2–4% (by weight)

emulsifiers, such as sodium dioctyl sulphosuccinate, sorbitan monooleate etc., can increase the rate of alkaline hydrolysis of esters like tridecyl formate by as much as 14 times. Menger (1979) has reported that the alkaline hydrolysis of benzotrichloride is also enhanced in the presence of emulsifiers.

3.5 Role of wetting and dispersing agents in solid-liquid systems

Surface active agents have been used to increase rates of solid-liquid reactions because of their ability to wet the solid surface and hence effect better dispersion of solids in the liquid phase. Levenson (1954) has shown how the reaction rate between flowers of sulphur and sodium sulphite solution (which is very slow due to the failure of the sulphur to wet and make good contact with the sulphite) can be enhanced by using ionic and non-ionic wetting agents. The primary stage of the reaction is the attack of the SO_3^{2-} ion on the surface of the sulphur and hence a cationic agent should give added enhancement as it would leave the surface of the sulphur with a positive charge. By assuming the enhancement (~ 4) by a non-ionic agent to be solely due to the dispersion effect, it was observed that enhancements by cationic agents are twice that by non-ionic ones, whereas anionic detergents retard the specific reaction rate per unit surface area and hence enhancement is half of that by nonionic detergents.

3.6 Hydrotropy

A hydrotropic agent is one which increases the solubility of hydrophobic substrates in the aqueous phase. Hence rates of solubility limited heterogeneous reactions are expected to increase in the presence of hydrotropes.

Common hydrotropes include urea, glycols, aromatic sulphonic acids and their sodium salts, polymers like polyacrylic acid, poly vinyl alcohol etc.

Some postulated mechanisms regarding the mode of hydrotropic solubilisation include hydrogen bonding, complex formation with hydrophobic substrate (Korenman 1974) and incorporation of hydrophobic substrate into the hydrophobic cavities of aggregates of big molecule hydrotropes (Okubo *et al* 1973). The hydrotropic action generally occurs at high concentrations of hydrotropes (20–40% by weight) and hence there could be significant changes in the properties of the aqueous phase such as viscosity, ionic strength etc.

McKee (1946) has reviewed potential applications of hydrotropy in electrochemical reactions. The Cannizaro reaction of benzaldehyde with NaOH has been reported to be considerably enhanced in the presence of sodium cymene sulphonate. Hydrotropic solutions of sodium cymene sulphonate have also been used in the selective extraction of aniline from an aniline-dimethylaniline mixture. Application of hydrotropy to dissociation extraction (separation of close boiling acidic/basic substances by exploiting differences in their dissociation constants (Wadekar & Sharma 1981), may give some interesting results.

Janakiraman & Sharma (1985c) have observed that rates of solid-liquid alkaline hydrolysis of phenyl benzoate and ethyl *p*-nitrobenzoate were enhanced 2 to 17 times in the presence of sodium salts of *p*-toluene sulphonic acid, 2,4-dichlorophenol and 2,4,6-trichlorophenol. They have also observed that the solubility of *p*-cumyl phenol in aqueous solutions containing 50% *p*-toluene sulphonic acid was 350 times higher than that in water.

3.7 Operation under refluxing conditions for liquid-liquid systems

Operation under refluxing conditions results in higher mass transfer rates because of increased interfacial areas particularly when the dispersed phase is being refluxed.

An added advantage of this strategy is in liquid-liquid reacting systems which are highly exothermic where refluxing may serve as a convenient means of heat removal.

Bhave & Sharma (1981) have shown that interfacial areas can increase by 40–90% under refluxing conditions by studying the reduction of *m*-nitrochlorobenzene with aqueous sodium disulphide and the alkaline hydrolysis of tridecyl formate.

3.8 Slurry reactors: Use of particles smaller than the diffusion film thickness

The presence of fine particles in the diffusion film can significantly affect the rates of both slow and fast reactions.

Ramachandran & Sharma (1969) showed theoretically how the rates of gas absorption accompanied by an instantaneous reaction in fine particle slurries can be significantly enhanced when these particles are present in the film. The significant dissolution of these particles in the film increases the local concentration of the reacting species and hence enhances reaction rates. Sada *et al* (1979) have obtained enhancements of 2–6 times in the absorption of SO₂ in lime and CaCO₃ slurries.

Recently, Pal *et al* (1982) have shown how the presence of fine catalytic carbon particles (1.7 and 4.33 μ) in the film can enhance the rates of even fast reactions, such as oxidation of Na₂S, by a factor of as much as 10.

More recently Janakiraman & Sharma (1985b) have shown how fine carbon particles, because of their affinity for hydrophobic compounds, can increase rates of solubility limited heterogeneous reactions. The hydrophobic organic substrate is adsorbed on the carbon surface and allowed to react with the aqueous phase reagent. Enhancement factors of 2–4 have been obtained in the oxidation of cyclododecanone and hydrolysis of phenyl benzoate and ethyl *p*-nitrobenzoate.

The role of micelles, which are also small enough to be present in the film, has already been discussed earlier.

Table 1 summarises the role of fine particles, smaller than diffusion film thickness, in multiphase systems.

3.9 Microemulsions

Microemulsions are colloidal dispersions consisting of monodisperse droplets of water in oil (w/o) or oil in water (o/w). The droplet sizes are of the order of 100 Å dia and hence these clear, stable fluids offer a large oil-water interfacial area and can contain upto 30% of the dispersed phase. Microemulsions are excellent candidates for serving as reaction media as they can solubilise both polar and non-polar reagents and the large interfacial area allows easy contact between organic and aqueous phase reagents. Microemulsions with and without detergents have been considered though the latter have the clear advantage of easier separation and removal of product.

A number of reactions such as acid base reactions, formation of metalloporphyrins and other complex ions, ester hydrolysis and some photochemical and electrochemical reactions have been studied in these media and the rates have been found to be competitive with those obtained in micellar and phase transfer catalyzed systems (Holt 1980; Mackay 1981). Gonzalez & Holt (1981) have used microemulsions for the synthesis of macrocyclic lactones with high selectivity.

Table 1. The role of particles smaller than the diffusion film thickness

Enhancement for some typical cases				
System	Case	$\phi = R_A$ with particles/ R_A without particles	Practical relevance	Reference
1. Absorption/extraction with reaction into a slurry containing sparingly soluble fine particles	Instantaneous reaction further enhanced e.g. absorption of lean SO_2 in aqueous slurries of lime/ CaCO_3 $\phi \sim 2-6$	$\frac{[B_s](D_B k_{sL} a_p)^{1/2}}{k_L [A^*] (1 + D_B [B_s]/D_A [A^*])}$	Solid dissolution in the film causes concentration of B to increase and hence rates of absorption are enhanced	Ramachandran & Sharma (1969); Sada <i>et al</i> (1979)
2. Fine catalytic particles in two phase reactions	Fast reaction further enhanced e.g. oxidation of Na_2S (G/L) in presence of fine catalytic carbon (1.7 μm , 4.33 μm size) $\phi \sim 2-11$	$\frac{[A^*](D_A k_w + D_A k_{sL} a_p)^{1/2}}{[A^*](D_A k_w)^{1/2}}$	Presence of catalyst particles in film causes even rates of fast reactions to be enhanced.	Pal <i>et al</i> (1982)
3. Fine particles-adsorbents for hydrophobic reactants (fine carbon particles; fine polymer particles etc.)	Fast reaction made faster e.g. alkaline hydrolysis (S/L) of ethyl- <i>p</i> -nitrobenzoate $\phi \sim 2-4$ Slow reaction made faster e.g. oximation of cyclododecanone (S/L) $\phi \sim 2-3$	$\frac{[A^*]\{D_A(k_w + K_c a_c)\}^{1/2}}{[A^*](D_A k_w)^{1/2}}$ $\frac{a_p [A^*]\{D_A(k_w + K_c a_c)\}^{1/2}}{[A^*]\{(1/k_{sL} a_p) + (1/k_w)\}^{-1}}$	Hydrophobic A is readily adsorbed and reacts on carbon surface; additional avenue for enhancing rates of solubility limited heterogeneous reactions	Janakiraman & Sharma (1985b)
4. Micellar catalysis	Fast reaction made faster e.g. oximation of cyclododecanone (L/L and S/L) $\phi \sim 3-70$ Slow reaction made fast e.g. alkaline hydrolysis of phenylbenzoate (S/L) using lauryl pyridinium chloride, CTAB etc. $\phi \sim 2-10$	$\frac{[A^*]\{D_A(k_w + I_m M_A M_B k_w)\}^{1/2}}{[A^*](D_A k_w)^{1/2}}$ $\frac{a_p [A^*]\{D_A(k_w + I_m M_A M_B k_w)\}^{1/2}}{[A^*]\{(1/k_{sL} a_p) + (1/k_w)\}^{-1}}$	Hydrophobic A readily solubilized by hydrophobic interior of micelles in aqueous phase; rates of solubility limited heterogeneous reactions drastically increased	Janakiraman (1984); Janakiraman & Sharma (1985a)

Martin *et al* (1982) have studied the reaction of benzyl chloride with bromide ion in water/oil microemulsions, made up of water, potassium bromide, hexane, cetyl trimethyl ammonium bromide and 1-butanol. It is reported that overall conversions are comparable to those obtained by the use of phase transfer catalysts.

Jaeger & Frey (1982), Jaeger & Ward (1982) and Martin *et al* (1984) have considered the use of destructible surfactants in detergent microemulsions where the surfactants are converted to non-surfactant products after reaction. This avoids any emulsification problems and facilitates removal of products. For instance, ketal-based surfactants have been prepared which are found to be as effective as cetyl trimethyl ammonium bromide. They are stable under neutral and alkaline conditions but can be converted to non-surfactant products in the presence of acid (Jaeger & Frey 1982).

An interesting application of microemulsions could be in the field of polymerisation. It has been found possible to prepare detergentless microemulsions containing styrene monomer. The use of persulphate as an initiator was observed to give a solid plug of polymerized styrene (Holt 1980). However, the work on microemulsions as reaction media is still in the very early stages and there is a lot of scope in the field. Fourre *et al.* (1983) report that the extraction of Ga(III), at levels of 0.004–0.012 M from aqueous solutions containing 3.5 M NaOH and 1.5 M Al(III), into kerosene increases upto 20 times by addition of long chain alcohols and sodium salts of long chain carboxylic acids. The organic phase of this system has been shown to be a water/oil microemulsion.

3.10 Catalysis by surfactant stabilized foams

In a recent publication, Sviridov & Azarova (1983) have reported some interesting results for the hydrolysis of 2,4-dinitrochlorobenzene carried out at the solution-gas interface in the presence of cationic surfactants. Here a foam was prepared by dispersing air through an aqueous solution containing NaOH and a cationic surfactant (present at concentrations below the critical micelle concentration so as to exclude any micelle formation) and contacted with 2,4-dinitrochlorobenzene. It is reported that the enhancements in rates were higher than that obtained in micellar solutions (where enhancements of upto 40 have been observed).

The reason for the enhancement in reaction rates in the surface layers at the solution-gas interface is similar to that for micellar catalysis. Hydrophobic forces cause a concentration of 2,4-dinitrochlorobenzene in the apolar regions of the surface surfactant layers in the foam film whereas electrostatic attractions ensure the presence of hydroxyl ions.

These results are indeed very interesting and deserve further study. It would also be interesting to see how the presence of fine carbon particles in these foams can effect reaction rates.

3.11 Use of some novel substances for enhancing rates

Patents taken by Exxon (Kramer 1982a, b) claim that aminoalkyladamantane (AAA) can enhance rates of the alkylation reaction of isobutane with isobutene/butanes and isomerisation of alkanes (which are catalyzed by concentrated sulphuric acid). Thus a 0.05 M concentration of AAA was reported to enhance reaction rates by a factor of 7.

More recently, Exxon (Kramer 1984) claimed that the isomerization rates of C₄–C₆ paraffinic hydrocarbons in concentrated sulphuric acid were enhanced by a factor of 7 in the presence of 0.002 M adamantyl carboxylate and/or an adamantyl sulphonate catalyst.

Hirai & Komiyama (1981) have claimed that the reaction of phenol with chloroform and aqueous NaOH gives 46 % yield of 4-hydroxy benzaldehyde as compared to 15 % when α -cyclodextrin is not used. The role of cyclodextrin in two-phase free radical polymerizations will be discussed later.

Molecular sieves have also been used as catalysts in homogeneous systems. Bakke *et al* (1982) have shown that montmorillonite catalyses the chlorination and nitration of toluene. Nitration gives 56 % *p*- and 41 % *o*-derivative.

4. Excursions from one multiphase system to another

4.1 Gas-liquid (G/L) to liquid-liquid (L/L)

Liquid-liquid systems can provide very large interfacial areas ($> 100 \text{ cm}^2/\text{cm}^3$) as compared to gas-liquid systems ($< 10 \text{ cm}^2/\text{cm}^3$). Hence if process conditions for solutes having normal boiling points in the range of -20 to $+20^\circ\text{C}$ can be altered from the gas-liquid mode to the liquid-liquid mode, we can benefit by realising higher volumetric rates. This assumes that mass transfer resistance is confined to the phase in which the reaction occurs.

Thus, for instance, the selective removal of isobutylene from C_4 fractions by contacting with 50–60 % H_2SO_4 can benefit by changing from the gas-liquid mode to the liquid-liquid mode. This can be achieved by suitably raising the pressure.

Similarly the removal of COS from the C_3/C_4 fractions from associated gases, cat-cracker gases etc. would also benefit if we change to the liquid-liquid mode by manipulating the system pressure. An additional advantage of switching over to the liquid-liquid mode is that rates may be further enhanced by use of PTC and emulsifiers. Bhavé & Sharma (1983) have shown that the extraction of COS from *n*-heptane into an aqueous phase containing NaOH is enhanced as much as 25 times when Aliquat 336 (triocetyl methyl ammonium chloride) is used as a PTC.

4.1a Adoption of supercritical conditions: An interesting situation may arise when a particular reaction may be amenable for operation under supercritical conditions. Consider the case of liquid phase oxidation of isobutane to *t*-butyl hydroperoxide which is conducted in industrial practice on a very large scale. Here a recent patent (Baumgartner 1983) has claimed that supercritical conditions can be adopted by working at temperatures ($\sim 165^\circ\text{C}$) and pressures ($\sim 91 \text{ atm}$) above critical conditions. We do not know what happens to the rate per unit volume as well as selectivity in such cases but we may well have very favourable results.

Ahmed *et al* (1984) have claimed in a recent patent that alkanolamines containing a high percentage of monoalkanolamines were prepared from 2–4 C alkylene oxide and ammonia at temperatures greater than 100°C and a pressure high enough to maintain the reaction in a supercritical fluid phase.

Further, many multiphase reactions are limited by low solubilities of reacting solutes and hence we may benefit by resorting to operation under supercritical conditions in such cases. For instance, the absorption of propylene in aqueous solutions of sulphuric acid may benefit by enhanced solubilities of propylene under supercritical conditions ($P_c = 46 \text{ atm}$).

The supercritical conditions for Cl_2 are also quite reasonable ($P_c = 76 \text{ atm}$, $T_c = 417^\circ\text{K}$) and may be employed in the chlorination of dissolved phenolic materials in the aqueous phase.

4.2 Liquid-liquid (L/L) to gas-liquid (G/L)

Liquid-liquid reactions may benefit from a switchover to gas-liquid reactions when the mass transfer resistance and reaction occur in different phases. The liquid phase in which mass transfer resistance exists may be converted to a gaseous phase to take advantage of the higher values of mass transfer coefficient in gaseous phase compared to that in the liquid phase.

4.3 Gas-liquid (G/L) to gas-liquid-liquid (G/L/L)

Sharma (1983) has discussed the advantages of using an additional liquid phase. This second liquid phase can show very high solubility for the solute gas and therefore can enhance rates of mass transfer. The recent work of Mehra & Sharma (1985) shows that the absorption of isobutylene in aqueous sulphuric acid solutions increases 2–11 times when an emulsion of chlorobenzene in the aqueous phase is used. The second liquid phase can also act as a reactant or as an extractant for the reaction intermediates and lead to increased selectivities.

4.4 Liquid-liquid (L/L) to gas-liquid-liquid (G/L/L)

In some cases, liquid-liquid reactions may be deliberately carried out under refluxing conditions where it becomes a gas-liquid-liquid system.

Vaporisation of one of the phases serves in the heat removal of highly exothermic reactions such as nitration of benzene, toluene etc.

We have discussed earlier how operation under refluxing conditions can increase interfacial areas and hence offers definite advantages in switching over from liquid-liquid to gas-liquid-liquid systems.

4.5 Solid-liquid (S/L) to liquid-liquid (L/L)

When the melting points of sparingly soluble solids are in an acceptable range, we might switch over from solid-liquid to melt (liquid)-liquid systems to enjoy the benefit of larger interfacial areas in liquid-liquid systems.

Added benefits of this switchover include the use of PTC in some cases such as ester hydrolysis. Operation under refluxing conditions and use of emulsifiers would serve to increase rates through an increase in interfacial area. Further if the solubility increases with temperature it will further increase rates.

In the oximation of cyclododecanone it was observed that the specific rate of reaction increases nearly 25 times when we switchover from a solid-liquid reaction at 28°C to a melt liquid reaction at 90°C. This increase is due to the increase in both the solubility as well as the rate constant. In the micellar catalysis of oximation of cyclododecanone (m.p. 59°C), it was observed that at 90°C in a melt/liquid system, sodium lauryl sulphate in addition to forming micelles, also acted as an emulsifier and further enhanced rates by a factor of 2–3 under otherwise similar conditions (Janakiraman & Sharma 1985a).

The reduction of *m*-nitrochlorobenzene with aqueous sodium disulphide carried out under refluxing conditions as a melt-liquid system is an example of a case, where in addition to the increase in interfacial area obtained by switching over from a solid-liquid to a liquid-liquid system, further enhancements (40–90%) are obtained by operating under refluxing conditions (Bhave & Sharma 1981).

4.6 Liquid-liquid (L/L) to solid-liquid (S/L)

Phase separation problems often set an upper limit to interfacial areas obtainable in liquid-liquid systems. A very unusual way of overcoming this handicap has been suggested in the disproportionation of elemental phosphorous by reaction with water to phosphine and phosphoric acid where a special liquid-liquid-solid technique has been used for this purpose (Harnisch 1980). Liquid white phosphorus is emulsified in phosphoric acid and first converted to very fine particle solid red phosphorus. This in turn is converted into phosphine and phosphoric acid in the subsequent solid-liquid reaction.

4.7 Liquid-liquid (L/L) to liquid-liquid-solid (L/L/S)

A number of liquid-liquid reactions, such as hydrolysis, esterification, alkylation etc., are catalysed by PTC. To overcome problems of removal of PTC, we may immobilize these catalysts on polymeric and non-polymeric supports (solid supported phase transfer catalysis) (Regen 1975, 1979). In many cases the PTC itself may be polymeric such as quaternized polyvinyl pyridine.

Similarly, two-phase liquid-liquid reactions catalysed by enzymes may also be converted to a three-phase liquid-liquid-solid system by immobilizing enzymes on solid supports.

We can also have situations where a liquid phase reactant is bound on a solid matrix to avoid product contamination. For instance, dissolved oxygen in H_2O can be treated with ion exchange resins having hydrosulphite ions which react rapidly with O_2 and the product water (high quality boiler feed H_2O) can be free of any dissolved salt (Martinola 1980).

4.8 Gas-solid catalysed to gas-melt catalysed

A number of reactions which are catalysed by solid catalysts can also be carried out in melts containing the active ingredients of the catalyst. For instance, the oxidation of SO_2 to SO_3 in the presence of V_2O_5 catalyst can be carried out in melts of potassium pyrosulphate containing V_2O_5 . Because of the high heat transfer coefficients offered by molten salts, the removal/supply of heat can be conveniently carried out. This would mean that the problem of hot spots and catalyst deactivation can perhaps be avoided. Further, problems of catalyst fouling would be practically nonexistent. However, as cautioned earlier (§1) the molten catalyst system is unlikely to be industrially attractive for common solid-catalyzed vapour phase reactions (except where temperature control is very critical) in view of the relatively low active areas provided by the melt system compared to that offered by the porous catalyst. It may then become attractive to distribute the melt in the pores of the catalyst (Kenney 1975).

For the manufacture of nitropropane (an intermediate for drugs and other chemicals), the use of molten nitrates ($NaNO_3 + KNO_3$) in the temperature range of $372-444^\circ C$ is likely to offer advantages over vapour phase nitration because of better temperature control achievable in the molten-salt medium (Coldiron *et al* 1958). It is important to create conditions for uniform temperature, since these reactions are hazardous and may cause an explosion.

The vapour phase oxidation of HCl (Deacon's process) requires relatively high temperature ($400-500^\circ C$). Since this reaction is exothermic and limited by equilibrium factors, it would be better to work at lower temperatures where higher equilibrium

conversions can be obtained. It is possible to convert HCl to Cl_2 in molten salts containing $\text{CuCl}-\text{CuCl}_2$ or $\text{CuCl} + \text{CuCl}_2 + \text{KCl} + \text{LiCl}$. The data of Ruthven & Kenney (1968) indicate that the reaction rate is controlled by the rate at which the melt can absorb oxygen.

5. Improving selectivity by using an additional liquid phase

The purpose here is to deliberately impose an additional inert, non-volatile liquid phase which shows a very high distribution coefficient for the desired intermediate product. The intermediate product is thus protected from undergoing further reactions resulting in high selectivity.

4-nitroalkanoic acids (useful as intermediates for insecticides, amino acids etc.) are usually made by a Michael addition reaction between nitroalkanes and acrylic esters in a homogeneous medium in the presence of soluble organic bases. However, the yields are low as disubstitution also occurs. If we now switch over to a two-phase system consisting of dichloromethane (containing reactants) and an aqueous phase containing NaOH, the yield of the desired product can be raised. The reaction occurs in the aqueous phase but the intermediate has a high distribution coefficient in favour of the organic phase (Chasar 1982).

Use of an additional liquid phase in slurry reactors can also increase selectivity (Koopman *et al* 1981). For instance, hydrogenation of styrene oxide in a slurry reactor with Raney Ni as the catalyst yields essentially phenylethyl alcohol as the product in the presence of a fairly large amount of water. By contrast, in the absence of water, the product is essentially phenylmethyl carbinol under otherwise similar operating conditions.

Liquid membrane technology is a case of a liquid-liquid-liquid extractive reaction and has been used in the field of waste-water treatment, separation of hydrocarbons, metal ions etc. (Li 1978; Marr & Kopp 1982). Liquid membranes can be of the multiple emulsion type or in the form of a thin film supported on a solid structure. In the latter case the liquid is impregnated into the pores of a solid membrane such as a flat polymer sheet, spiral wound or hollow fibre type. The multiple emulsion type membrane is obtained by dispersing an emulsion of two phases into a third phase and may be of the o/w/o or w/o/w type. The material to be recovered from the outer phase, diffuses through the membrane phase and is trapped by reaction in the inner phase. A carrier may be used to facilitate transport.

A lot of work has been done in the use of multiple emulsion liquid membranes to recover phenol, Cu^{2+} , Cr^{6+} ions etc., and in the separation of olefin/aliphatic mixtures (Li 1978; Marr & Kopp 1982).

It has been reported (Parkinson *et al* 1983) that the extraction of uranium from wet process phosphoric acid by using multiple emulsion liquid membranes can cut the capital costs by about 40% as compared to that of a conventional solvent extraction unit. Here the membrane phase consists of di-(2-ethylhexyl)phosphoric acid, trioctyl phosphine oxide (both as carriers) and a surfactant dissolved in a hydrocarbon solvent.

Ammonia from aqueous solutions has been successfully removed by trapping it as NH_4^+ ions in the encapsulated droplets by reaction with H_2SO_4 (Kitagawa *et al* 1977). The use of boric acid may also be considered here. The ammonium borate formed could be heated to regenerate ammonia and the boric acid could be recycled.

It has been claimed that polysulphone hollow fibres, with 60–80% porosity, can be

impregnated with 30% (by volume) Kelex in a hydrocarbon oil and used to recover copper ions. In a typical case, an aqueous solution containing 0.2 wt% Cu at pH 2.7 was successfully treated (Bend Research Inc., 1980).

Polysulphone hollow fibre membranes impregnated with an amine-kerosene mixture have been used to extract uranium (present as uranyl sulphate in leached solutions). The leach solution is pumped down the bore of the hollow fibres and the amine complexes with the uranyl sulphate. This complex diffuses across the membrane. At the outer surface of the hollow fibre wall the uranyl sulphate is stripped with a sodium carbonate solution from the amine which then returns to the inner side to repeat the cycle. It has been estimated that a commercial plant would need only one-tenth of the amine volume as compared to an equivalent solvent extraction plant (Parkinson *et al* 1983).

Attempts are being made to develop supported liquid membranes to remove transuranic and fission products from plutonium production waste streams. Polymers that can stand the relatively low radiation levels of this process are being tried (Parkinson *et al* 1983).

Liquid membranes have also been used as a reaction media. Thus catalytic oxidation of ethylene to acetaldehyde is possible by forming a liquid membrane encapsulated bubble which contains oxygen and C_2H_4 . The liquid membrane is the catalyst phase which contains an aqueous $PdCl_2/CuCl_2$ solution, the viscosity of which is increased with glycol for stability reasons. The reaction occurs in the membrane phase and the product acetaldehyde is extracted into the outer phase which is solvent 3-heptanone (Holwachs & Schuglerl 1980).

Liquid membranes have also been used in the separation of gaseous mixtures. These can be in the form of immobilized liquid films impregnated in the pores of porous polymer membrane or may be supported through formation of foam (Sirkar 1980).

H_2S can be selectively removed from coal gasifier gases containing CO_2 and H_2 by using a liquid membrane of aqueous carbonate solution at temperatures of 90–130°C impregnated in the pores of porous membranes. Though both CO_2 and H_2S diffuse, the reaction of H_2S with the carbonate is very fast as compared to that of CO_2 . Separation factors as high as 300 may be obtained (Matson *et al* 1977).

Li & Asher (1971) have shown that liquid membranes can be used in blood oxygenation. Here O_2 is bubbled through fluoro-carbon solutions containing surfactants. These oxygen bubbles which are now surrounded by stable fluorocarbon membranes are contacted with blood. The oxygen from within diffuses into the blood whereas the CO_2 diffuses from the blood to the bubbles.

Reports indicate that it is possible to get 80% oxygen from air by use of a metal ion complexing carrier that can bind the oxygen selectively and reversibly. The complex breaks up at the lower pressure side after diffusing through the membrane and the carrier returns (Parkinson *et al* 1983).

The use of macrocyclic compounds, like cyclic polyethers, as carriers, has good potential. Here the addition of donor atoms can increase their affinity for a particular metal (Parkinson *et al* 1983).

6. Simultaneous absorption/extraction: kinetic vs equilibrium factors

In a number of industrial operations it may be necessary to selectively absorb/extract a substance from a mixture. Thus, for instance, it may be necessary to remove phosgene

from process gas streams which also contain CO_2 (Ramachandran & Sharma 1970, 1971). The reaction of phosgene with water is as follows:

When the gas mixture of phosgene and carbon dioxide is absorbed in water, the presence of CO_2 does not affect the absorption rate of phosgene. However, the concentration of CO_2 in the liquid film is increased due to the hydrolysis of phosgene and consequently the absorption rate of CO_2 is severely lowered in the presence of phosgene. Thus in aqueous solutions of soda ash, under certain conditions, no CO_2 will be absorbed even though there is a net driving force from bulk gas to bulk liquid phase.

Ramachandran & Sharma (1971) have discussed various aspects of simultaneous absorption of H_2S and CO_2 . The absorption of H_2S in amines and aqueous ammonia solutions is accompanied by instantaneous reaction of H_2S with amines/ammonia. When the partial pressure of H_2S is relatively low and the concentration of amine high, then the resistance to mass transfer may even shift from the liquid phase to the gas phase. The reaction of CO_2 with amines/ammonia, on the other hand, has a finite value of rate constant. This difference in kinetic rates may be exploited for selective removal of H_2S from $\text{H}_2\text{S}/\text{CO}_2$ mixtures.

Aqueous ammonia solutions are sometimes employed to remove H_2S selectively particularly in the coke oven industry. High selectivity may be obtained for H_2S if we go in for contactors which give high values of liquid side mass transfer coefficient, k_L (e.g. plate contactors). Here the reaction of ammonia with H_2S occurs entirely in the film whereas that with CO_2 occurs only in the bulk and is insignificant. Thus selectivity decreases drastically when we switch over to a packed column where k_L is low and reaction of CO_2 with NH_3 becomes significant in the film.

In the absorption of C_4 fractions in sulphuric acid, the use of 50–55 % sulphuric acid gives high selectivity for isobutylene. Here the reaction of isobutylene with sulphuric acid occurs in the film and that of 1- and 2-butenes occurs in the bulk and is insignificant. When sulphuric acid solutions of higher strengths are used, both reactions occur in the film and the selectivity with respect to isobutylene falls (Ramachandran & Sharma 1971).

In the simultaneous extraction of Cu^{2+} and Fe^{2+} ions by oximes, both the metal ions can form complexes with the oximes and selectivity with respect to Cu^{2+} is not realised when contact times are very long. However, the reaction of Cu^{2+} is much faster and hence the use of short contact times would dramatically improve selectivity for Cu^{2+} ions (Doraiswamy & Sharma 1984).

Thus a careful consideration of kinetic, equilibrium and hydrodynamic factors is necessary to obtain high selectivities when simultaneous absorption/extraction is involved.

7. Heterogeneous reactions in biocatalysis

Conducting certain enzyme-catalysed reactions in two-phase systems has a number of engineering and thermodynamic benefits (Kastanek *et al* 1982; Martinek & Semenov 1981; Andersson *et al* 1983).

- (i) Substrate insoluble in the aqueous phase can be used by dissolving them in the second immiscible organic phase (e.g. selective reduction of 20-keto steroids to 20-hydroxy steroids).
- (ii) Prevention of enzyme denaturation by the organic substrate and solvent as the enzyme remains in the aqueous phase.
- (iii) Thermodynamic benefits are immense since the overall equilibrium constant for an enzymic transformation in a two-phase heterogeneous system can be very favourable as compared to that for a single phase.
- (iv) Ionic dissociative reactions (in acid/base systems) can be suppressed.
- (v) pH conditions favourable to enzyme stability and optimality can be produced without adversely affecting the reaction thermodynamics.
- (vi) No activity is lost as in immobilization on solid matrix.

The synthesis of some complex esters and amides in two-phase systems has been studied (Martinek & Semenov 1981).

Andersson *et al* (1983) have also brought out these advantages in the extractive deacylation of benzyl penicillin.

A lot of interest has been focussed on the synthesis of artificial enzymes. Efforts are also being made to mimic the shape selectiveness of enzymes as a result of which only certain molecules are immobilized on its surface and only the desired reaction takes place in the desired geometry (Fendler 1984). Synthesis of large molecules with surfaces that can be shaped to accommodate a desired reactant is being tried.

Enantioselective hydrolysis of amino acid esters by chiral bilayer membranes has received good attention in biomimetic chemistry. In a recent report, Ohkubo *et al* (1984) have reported that the enantioselective hydrolysis of dipeptide type amino acid esters by di or tripeptide nucleophiles in the bilayer vesicular aggregates of didodecyldimethylammonium bromide resulted in the enantiomer rate ratio of $LL/LD = 1.1$ to 18 . This could be further enhanced to 36 by lowering the temperature from 25 to 10°C .

In another recent study (Anon 1984) *N-p*-trifluoromethyl benzyl cinchonium bromide was used as a phase transfer catalyst in the conversion of 6,7-dichloro-5-methoxy-2-phenyl-1-indanone to the *S*(+)-2-methyl derivative with methyl chloride. Enantiometric excesses were as high as 92% with 95% yields. This one-step process eliminates the need for multistep synthesis for obtaining these optically active compounds in high enantiometric excesses.

Woodruff (1983) has discussed methods to overcome self-inhibition of reaction in the synthesis of antibiotics where the antibiotics formed are strong enough to kill the microorganisms producing them. In the production of novobiocin, a selective resin is added to the fermentation tank. This resin removes the novobiocin antibiotic as it is being formed and hence higher yields are realised. This is yet another example of how a change-over to a multiphase system can prove beneficial.

8. Recovery of gases through slurry absorbents

We usually employ liquid phase (aqueous and non-aqueous) absorbents for removal/recovery of solutes. There are special circumstances when slurries are used (as a part of reaction systems, slurries are frequently encountered, Doraiswamy & Sharma 1984). The well-known example of SO_2 absorption in slurries of lime/magnesia/

limestone can be cited (Sada *et al* 1979).

A special case is that of hydrogen and merits attention as homogeneous liquid phase absorbents, which react reversibly, have not yet been developed. Processes have been patented for the selective removal of H_2 from a mixture of gases by contacting the gas stream with a continuous stream of a hydride forming absorbent material (Parkinson 1982; Beenackers *et al* 1983). The material is in the form of particles kept in suspension in a fluid medium. Lanthanum-nickel alloy or other alloys of rare earth group metals with Ni or palladium have been suggested. The reaction is reversible at very convenient temperatures and hydride particles can be thermally decomposed to liberate H_2 . Gaseous streams containing as low as 15% hydrogen can be treated, and for lean streams these have clear advantages over cryogenic or molecular sieve-based processes.

9. Two-phase free radical polymerisation

9.1 Cyclodextrin catalysis

Cyclodextrin is the name of a class of cyclic oligomers of glucose whose members are α -(hexamer), β -(heptamer), γ -(octamer) cyclodextrin etc. Like enzymes they have a hydrophobic cavity, satisfactory solubility in water and sites for introduction of catalytic groups (Saenger 1980; Tabushi 1982). Crystallographic studies indicate that water molecules occupy the hydrophobic cavity in the absence of a 'guest' molecule. However, when a specific 'guest' molecule is added to the cyclodextrin solution, it drives out the water molecule and occupies the cavity by itself due to hydrophobic interactions. β -cyclodextrins are known to promote two-phase free radical polymerisation of water-soluble vinyl polymers such as acrylamide, sodium *p*-styrene sulphonate, acrylic acid etc., initiated by water-insoluble free radical initiators such as azo or peroxide compounds and increase rates by nearly an order of magnitude (Taguchi *et al* 1983).

Because of the high lipophilic character of β -cyclodextrins and their ability to form a stable inclusion complex with organic compounds, the free radical initiator (or a radical species generated from the initiator) is entrapped by the lipophilic β -cyclodextrin in the organic phase and then efficiently transferred to the aqueous phase to initiate the polymerization of the water-soluble vinyl monomers.

Recently Kunieda *et al* (1984) have shown that the two-phase polymerization of water-insoluble vinyl monomers, which have an aryl group, using water-soluble free radical initiators is also accelerated by the addition of lipophilic β -cyclodextrins. Here the suggested mechanism is that since β -cyclodextrin compounds can form a stable inclusion complex with the organic compounds and can stabilize radicals which are generated in their hydrophobic cavity, it is quite possible that the lipophilic β -cyclodextrin traps a vinyl monomer in its hydrophobic cavity in the organic phase and transfers it to the aqueous phase to react with a water-soluble initiator and then takes a monomer radical generated in the cavity again to the organic phase to initiate the polymerization. It was observed that free radical polymerisation rates of benzyl methyl acrylate and phenyl methyl acrylate, initiated by inorganic initiators like $K_2S_2O_8$ and $(NH_4)_2S_2O_8$ were enhanced 2–3 times in the presence of β -cyclodextrins.

The special properties of cyclodextrins are largely retained when they are linked

together to form polymers which are insoluble when the degree of polymerization is sufficiently high. Cyclodextrins can also be bound to polymeric resins (Saenger 1980).

9.2 Phase transfer catalysis

The principle of PTC has also been used in two-phase free radical polymerization where an aqueous phase initiator is transferred to the organic phase containing a water insoluble monomer. Rasmussen & Smith (1981) have reported the enhancement in polymerization of vinyl monomers using PTC. They have studied the polymerization of butyl acrylate with $K_2S_2O_8$ in aqueous systems using crown ethers as PTC (e.g. 18-crown-6). Here the initiator $S_2O_8^{2-}$ is transferred to the organic phase as a complex with the crown ether.

The Minnesota Mining and Manufacturing Co. of the USA have patented a process for polymerization of ethyl acrylate by refluxing ethyl acrylate with an aqueous solution of $K_2S_2O_8$ using 18-crown-6 as a PTC (Rasmussen 1982).

10. Multiphase reactions in electrochemical cells

Manufacture of adiponitrile by electrohydrodimerization of acrylonitrile has made a big impact on organic electrochemical processes (Graft 1983). Electrochemical reactions in aqueous/organic dispersions are likely to be useful as PTC and emulsifiers may be used to speed up the reaction.

The anodic cyanation of naphthalene which involves aqueous cyanide solutions, has been carried out in the presence of PTC such as tetrabutyl ammonium hydrogen sulphate. The PTC helps in the transport of cyanide ion to the organic phase consisting of methylene chloride as a solvent. Oxidation of alcohol to aldehyde with hypobromite has also been studied in the presence of PTC (Pletcher 1982).

The electrochemical hypochlorination of allyl chloride (which is sparingly soluble in water) in dilute HCl solutions using a non-ionic emulsifier (polyoxyethylene sorbitan monolaurate) has been studied by Comninellis & Plattner (1982). The rate of mass transfer of allyl chloride into the aqueous phase was observed to increase as much as 180 times in the presence of emulsifier.

Anodic cyanations of dimethoxy benzenes and anisole in aqueous micellar solutions have also been carried out (Laurent *et al* 1982). The reaction was found to be catalysed by cationic micelles and inhibited by anionic and non-ionic micellar systems.

Gas-liquid reactions in electrochemical cells have also been studied, e.g. the conversion of propylene to propylene oxide with *in situ* generation and conversion of propylene bromohydrin (Boussoulengas *et al* 1979).

Kreysa & Kulps (1983) report a new method of purifying waste gas streams containing solutes like SO_2 , Cl_2 etc. The gas-liquid mass transfer was enhanced by an electrochemical reaction of the dissolved gas. A concentric packed-column absorber has been suggested using packing of a conducting material containing a central diaphragm tube with a counter electrode. The electrochemical reaction occurs at the surface of the packing. Chlorine gives HCl and SO_2 gives H_2SO_4 together with oxygen and hydrogen respectively. This method appears very promising as no liquid effluent is involved.

11. Special type of solid-liquid reactions: dyeing of cellulosic fabrics with reactive dyes

Reactive dyes are widely used for dyeing of a variety of cellulosic fibres. Here a reactive group in the dye reacts with cellulose O^- (cellulosate ions) and thus the dye becomes an integral part of the cellulose. This is a special case where, instead of solid dissolution accompanied by chemical reaction, we have uptake of a reactive species B on cellulose accompanied by chemical reaction. It has been shown that the steps of diffusion of dye into the cellulosic material and its reaction with cellulosate ion are parallel steps and the reaction falls in the regime between slow and fast reactions (Sumner & Weston 1963; Rattee & Breuer 1974; Peters 1975).

12. Reactions in multiphase systems involving non-Newtonian materials

Attention has been paid in recent years to the hydrogenation of polymeric particles, suspended/dissolved in suitable solvents, in the presence of Raney Ni or Pd/C catalysts (Falk 1976). A recent patent (Nippon Zeon Company 1982) discusses the hydrogenation of conjugated diene polymer in the presence of a hydrogenation catalyst supported on powdered silica with average particle size less than $10\text{ }\mu\text{m}$. The vulcanised polymer showed good physical properties. There is need for a systematic study of slurry reactors involving non-Newtonian materials.

In many polymerization reactions, a volatile species is generated along with the desired polymer. At high levels of conversion where the reversible reaction becomes limiting, the continuous removal of the volatile product can shift the equilibrium favourably and high conversions can be obtained.

Recently Ravindranath & Mashelkar (1984) have examined the finishing stages of polycondensation in polyethylene terephthalate synthesis. A number of volatile products, such as acetaldehyde, water etc. are formed as byproducts during the finishing stages. The main product of the forward reaction, viz. ethylene glycol needs to be removed rapidly in order to drive this reversible polycondensation reaction forward. Ravindranath & Mashelkar (1984) show how the generation of volatile byproducts actually helps in driving the main reaction forward by lowering the effective partial pressure of ethylene glycol.

Mashelkar (1984) has recently reviewed diffusional phenomena in reacting macromolecular media. Diffusional effects can be important both in heterogeneous and even in homogeneous systems. Diffusional effects in free radical polymerization, solution, melt and solid-state polycondensations and in Ziegler-Natta polymerizations have been reviewed.

13. Wastewater treatment

Parulekar *et al* (1982) have reviewed the various engineering aspects of the treatment of wastewater for the recovery of valuable components.

The most common method of treating aqueous waste streams is by biological oxidation using air or oxygen. However, in those cases where the COD (chemical oxygen demand) is high ($20\text{ to }200\text{ kg/m}^3$), as in the effluent from pulp and paper mills, it may be economical to employ wet air oxidation. Here it may be possible to generate energy by recovery of the exothermic heat generated in the oxidation reaction.

Supercritical water can also be used in wastewater treatment. It can serve as an oxidizing agent for hazardous waste materials and also as an extractant for extraction of organic materials.

14. Choice of contactor

The type of reactor used can greatly influence the product distribution. In the oxidation of butane the ratio of the major products, acetic acid and methyl ethyl ketone (MEK), can be varied from 10:1 to 0.5:1 by decreasing the extent of backmixing. Thus acetic acid is the major product in a continuously operated agitated contactor where liquid is backmixed. On the other hand in a plug flow reactor (e.g. a pipeline reactor) the ratio of acetic acid to MEK is 1:1 (Saunby & Kiff 1976).

The absorption of chlorine in aqueous solutions of sodium hydroxide with simultaneous desorption of HClO (used in the production of high purity sodium hypochlorite and other chemicals) is of considerable practical interest. Lahiri *et al* (1983) have shown that the desorption of HClO is gas-film controlled. Hence the rate of desorption of HClO and the yield of HClO increases with increasing value of the gas phase mass transfer coefficient (k_G) and a lower value of k_L . Hence the use of contactors, such as a spray column, which gives relatively high values of k_G and low values of k_L is expected to be beneficial. By contrast a bubble column, which gives reasonably good values of both k_G and k_L , will be expected to give lower yields of HClO. Similarly, if the product is required as solid particles a spray absorber reactor would be ideal (e.g. NH_4NO_3 manufacture).

15. Simulation and modelling of multiphase contactors

Doraiswamy & Sharma (1984) reviewed the various types of contactors for multiphase systems encountered in practice. They have also given procedures and criteria for selection of the type of reactor needed for any particular application.

When the physicochemical data for the system are available it may be possible to predict the rates in any industrial equipment. The use of model contactors such as stirred cells, laminar jets, stirred contactors etc., have proved to be very useful in obtaining information necessary for scale-up. Danckwerts & Sharma (1966), Charpentier & Laurent (1974), Danckwerts & Alper (1975), Alper & Danckwerts (1976), and Laurent *et al* (1980), have considered several aspects of simulation and modelling of industrial contactors. Juvekar & Sharma (1977) have considered the design of some gas-liquid contactors. Recently Vasudevan & Sharma (1984) have discussed some aspects of the design of liquid-liquid reactors.

An interesting example of simulation of gas-liquid reactors is provided by absorption of lean and rich NO_x in aqueous solutions of sodium hydroxide. Our object is to maximise the production of nitrite while obtaining a negligible amount of nitrate. A detailed analysis brings out some unexpected results (Carta 1984). An increase in temperature, under otherwise comparable conditions, can bring about a substantial improvement. For instance, raising the temperature from 25 to 75°C can increase the yield of nitrite from 75 to 95%. This situation arises from the fact that an increase in temperature leads to higher vapour pressure of water and hence higher concentrations of water in the gas phase which is conducive to higher rate of formation of HNO_2 in the

gas phase. Since an irreversible reaction occurs in the liquid phase, there is no free nitrous or nitric acid concentration in the aqueous phase. This exercise brings out the importance of a detailed analysis for problems of considerable practical relevance.

16. Conclusions

In many reaction systems it may be advantageous to change over from a homogeneous to a multiphase system.

There are several strategies for intensifying the rates of multiphase reactions such as phase transfer catalysis, micellar catalysis, emulsifiers, hydrotropy etc. In some practical situations, it may be beneficial to change over from one multiphase system to another.

The presence of fine solid particles (smaller than diffusion film thickness) in slurry reactors can significantly enhance reaction rates.

Selectivity and yields can be improved by use of an additional liquid phase.

Use of supercritical conditions may prove very beneficial in some specific cases.

Multiphase reactions offer some unique advantages for biochemical and electrochemical reactions.

There is great scope for further work which is academically very interesting and is practically relevant.

References

- Ahmed M, Nelson J R, Gibson C A 1984 EP 100, 373 *cf* 1984 *Chem. Abstr.* 100: 138590g
Alper E, Danckwerts P V 1976 *Chem. Eng. Sci.* 31: 599–608
Andersson E, Mattiasson B, Hahn-Hagerdal B 1983 *Acta Chem. Scand.* B37: 749–750
Anon 1984 *Chem. Eng. News* 62(5): 25
Bakke J M, Liasker J, Lorentzen G B 1982 *J. Prakt. Chem.* 324: 488–490
Baumgartner H J 1983 EP 76, 533 *cf* 1983 *Chem. Abstr.* 99: 38034w
Beenackers A A C M, Van Swaaij W P M, Willibrordus P M 1983 EP 94, 136 *cf* 1984 *Chem. Abstr.* 100: 9374r
Bend Research Inc. 1980 FR 2, 451, 764 *cf* 1982 *Chem. Abstr.* 97: 200168s
Bhave R R, Sharma M M 1981 *Trans. Inst. Chem. Eng.* 59: 161–169
Bhave R R, Sharma M M 1983 *Chem. Eng. Sci.* 38: 141–145
Bolden P L, Hoskins J C, Kings A D Jr 1983 *J. Colloid Interface Sci.* 91: 454–463
Boussoulengas A V, Ehdaie S, Jansson R F W 1979 *Chem. Ind. (London)* 670–672
Bunton C A 1979 *Catal. Rev. Sci. Eng.* 20: 1–56
Carta G 1984 *Ind. Eng. Chem. Fundam.* 23: 260–264
Charpentier J C, Laurent A 1974 *AIChE J.* 20: 1029–1031
Chasar D W 1982 *Synthesis* 10: 841–842
Coldiron D C, Albright L F, Alexander L G 1958 *Ind. Eng. Chem.* 50: 991–992
Cominellis Ch, Plattner E 1982 *J. Appl. Electrochem.* 12: 253–256
Danckwerts P V, Alper E 1975 *Trans. Inst. Chem. Eng.* 53: 34–40
Danckwerts P V, Sharma M M 1966 *Chem. Eng. (London)* No. 202 CE: 244–280
da Silva A T, Danckwerts P V 1968 *Proc. Symp. Tripartite Chem. Eng. Conf., Montreal (London: Inst. Chem Eng.)* p. 48–56
Dehmloew E V, Dehmloew S S 1980 *Phase transfer catalysis, Monographs in modern chemistry* (Weinham: Verlag Chemie) Vol. 2
Doraiswamy L K, Sharma M M 1984 *Heterogeneous reactions: analysis, examples and reactor design* (New York: John Wiley) Vol. 2
Falk J C 1976 *Catalysis in organic synthesis* (eds.) P N Rylander, H Greenfield (New York: Academic Press)
Fendler J H 1984 *Chem. Eng. News* 62(1): 25–38
Fendler J H, Fendler E J 1975 *Catalysis in micellar and macromolecular systems* (New York: Academic Press)
Fourré P, Bauer D, Lemerle J 1983 *Anal. Chem.* 55: 662–667

- Fukuoka S, Chono M, Kohno M 1984 *J. Org. Chem.* 49: 1458–1460
- Gonzalez A, Holt S L 1981 *J. Org. Chem.* 46: 2594–2596
- Graft G M 1983 *Chem. Eng.* 90(6): 14–19
- Harnisch H 1980 *Pure Appl. Chem.* 52: 809–824
- Hirai H, Komiyama M 1981 P C T Int. Appl. wo 8203073 *cf* 1983 *Chem. Abstr.* 98: 71670c
- Holt S L 1980 *J. Disp. Sci. Technol.* 1: 423–464
- Holwachs W, Schugerl K 1980 *Int. J. Chem. Eng.* 20: 519–528
- Hoskins J C, King A D Jr 1981 *J. Colloid Interface Sci.* 82: 260–263
- Ido T, Ohyama N, Goto S, Teshima H 1983 *Kagaku Kogaku Ronbunshu* 9: 58 *cf* 1983 *Chem. Abstr.* 98: 125171m
- Jaeger D A, Frey M R 1982 *J. Org. Chem.* 47: 311–315
- Jaeger D A, Ward M D 1982 *J. Org. Chem.* 47: 2211–2223
- Janakiraman B 1984 *Heterogeneous reactions* Ph. D. (Tech.) Thesis, University of Bombay
- Janakiraman B, Sharma M M 1982 *Chem. Eng. Sci.* 37: 1497–1503
- Janakiraman B, Sharma M M 1985a *Chem. Eng. Sci.* 40: 223–233
- Janakiraman B, Sharma M M 1985b *Chem. Eng. Sci.* 40: 235–237
- Janakiraman B, Sharma M M 1985c *Chem. Eng. Sci.* (in press)
- Januszkiewicz K, Alper H 1983 *J. Mol. Catal.* 19: 139–143
- Juvekar V A, Sharma M M 1977 *Trans. Inst. Chem. Eng. UK* 55: 77–92
- Kastanek F, Zahradnik J, Ocampo G 1982 *Collect. Czech. Chem. Commun.* 47: 3019–3026
- Kenney C N 1975 *Catal. Rev. Sci. Eng.* 11: 197–224
- Kitagawa T, Nishikawa Y, Frankenfeld J W, Li N N 1977 *Environ. Sci. Technol.* 11: 602–605
- Koopman P G J, Buurmans H M A, Keiboom A P G, van Bekkum H 1981 *Recl. Trav. Chim. Pays. Bas.* 100: 156–161
- Korenman Y I 1974 *Russ. J. Phys. Chem.* 48: 377–379
- Kramer G M 1982a *us* 4,357,482
- Kramer G M 1982b *us* 4,357,483
- Kramer G M 1984 *us* 4,424,387 *cf* 1984 *Chem. Abstr.* 100: 120496w
- Kreysa G, Kulps H J 1983 *German Chem. Eng.* 6: 325–336
- Krishnakumar V K, Sharma M M 1983 *Synthesis* 17: 558–559
- Kuneida N, Shiode S, Ryoshi H, Taguchi H, Kinoshita M 1984 *Makromol. Chem. Rapid Commun.* 5: 137–140
- Lahiri R N, Yadav G D, Sharma M M 1983 *Chem. Eng. Sci.* 38: 1119–1133
- Laurent A, Fonteix C, Charpentier J C 1980 *AIChE J.* 26: 282–287
- Laurent E, Rauriyar G, Thomalla M 1982 *Nouv. J. Chim.* 6: 515–517
- Lee D G 1982 *Oxidation in organic chemistry, Part D* (New York: Academic Press) Chap. 2, p. 147
- Lele S S, Bhavre R R, Sharma M M 1983a *Chem. Eng. Sci.* 38: 765–773
- Lele S S, Bhavre R R, Sharma M M 1983b *Ind. Eng. Chem. Process Des. Dev.* 22: 73–6
- Levenson G I P 1954 *J. Appl. Chem. (London)* 4: 13–18
- Li N N 1978 *J. Membrane Sci.* 3: 265–269
- Li N N, Asher W J 1971 *Adv. Chem. Ser.* 118: 1–14
- Mackay R A 1981 *Adv. Colloid Interface Sci.* 15: 131–156
- Markofsky S B 1983 *Belgium* 897,411 *cf* 1984 *Chem. Abstr.* 100: 15622m
- Marr R, Kopp A 1982 *Int. Chem. Eng.* 22: 44–60
- Martin C A, Golich T G, Jaeger D A 1984 *J. Colloid Interface Sci.* 99: 561–567
- Martin C A, McCrann P M, Angelos G H, Jaeger D A 1982 *Tetrahedron Lett.* 23: 4651–4654
- Martinek K, Semenov A V 1981 *J. Appl. Biochem.* 3: 93–126
- Martinola F 1980 *German Chem. Eng.* 3: 79–88
- Masheikar R A 1984 *Recent advances in the engineering analysis of chemically reacting systems* (ed.) L K Doraiswamy (New Delhi: Wiley Eastern) p. 497
- Matson S L, Herrick C S, Ward W J 1977 *Ind. Eng. Chem. Process Des. Dev.* 16: 370–374
- McKee R H 1946 *Ind. Eng. Chem.* 38: 383–384
- Mehra A, Sharma M M 1985 *Chem. Eng. Sci.* (in press)
- Menger F M 1979 *Pure Appl. Chem.* 51: 999–1007
- Neumann R, Sasson Y 1983 *Tetrahedron* 39: 3437–3440
- Nippon Zeon Company 1982 JP 57, 205,404 *cf* 1983 *Chem. Abstr.* 99: 39641d
- Ohkubo K, Ogata H, Yamaki K, Yamashika K 1984 *Makromol. Chem.* 185: 891–897
- Okubo T, Chen S, Ise N 1973 *Bull. Chem. Soc. Jpn.* 46: 397–400

- Pal S K, Sharma M M, Juvekar V A 1982 *Chem. Eng. Sci.* 37: 327–336
- Parkinson G, Short H, McQueen S 1983 *Chem. Eng.* 90(17): 22–27
- Parulekar S J, Sharma M M, Joshi J B, Shah Y T 1982 *J. Sep. Process Technol.* 4: 2–28
- Peters R H 1975 *Textile chemistry, The physical chemistry of dyeing* (Amsterdam: Elsevier) Vol. 3, p. 598
- Pletcher D 1982 *Chem. Ind.* 11: 358–362
- Ramachandran P A, Sharma M M 1969 *Chem. Eng. Sci.* 24: 1681–1686
- Ramachandran P A, Sharma M M 1970 *Chem. Eng. Sci.* 25: 1743–1750
- Ramachandran P A, Sharma M M 1971 *Trans. Inst. Chem. Eng.* 49: 253–280
- Ramamurthy V 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* 93: 635–646
- Rasmussen J K 1982 *US* 4,326,049 *cf* 1982 *Chem. Abstr.* 97: 24370z
- Rasmussen J K, Smith H K 1981 *J. Am. Chem. Soc.* 103: 730–731
- Rattee I D, Breuer M M 1974 *Physical chemistry of dye absorption* (London: Academic Press) p. 244
- Ravindranath K, Mashelkar R A 1984 *AIChE J.* 30: 415–422
- Regen S L 1975 *J. Am. Chem. Soc.* 97: 5956–5957
- Regen S L 1979 *Angew. Chem. Int. Ed. Engl.* 18: 421–429
- Ruthven D M, Kenney C N 1968 *Chem. Eng. Sci.* 23: 981–990
- Sada E, Kumazawa H, Butt M A 1979 *Chem. Eng. Sci.* 34: 715–718
- Saengar W 1980 *Angew. Chem. Int. Ed. Engl.* 19: 344–362
- Saunby J B, Kiff B W 1976 *Hydrocarbon Process Petrol. Refiner.* 55(11): 247–252
- Sharma M M 1965 *Trans. Faraday Soc.* 61: 681–688
- Sharma M M 1983 *Chem. Eng. Sci.* 38: 21–28
- Sharma M M 1984 *Frontiers in chemical reaction engineering* (eds.) L K Doraiswamy, R A Mashelkar (New Delhi: Wiley Eastern) Vol. 1, p. 155
- Sirkar K K 1980 Gas permeation and separation through surfactant liquid membranes—State of the art, presented at 73rd Annual Meeting of AIChE, Chicago, paper No. 74a
- Skrzewski J, Cichacz E 1984 *Bull. Chem. Soc. Jpn.* 57: 271–274
- Sridharan K, Sharma M M 1976 *Chem. Eng. Sci.* 31: 767–774
- Sumner H H, Weston C D 1963 *Am. Dyestuff Reporter* 52: 442–450
- Sviridov V V, Azarova V I 1983 *J. Appl. Chem. USSR* 56: 1031–1033
- Szeja W 1982 *Zesz. Nauk. Politech. Slask. Chem.* 720: 5–78 *cf* 1983 *Chem. Abstr.* 98: 126496h
- Tabushi I 1982 *Acc. Chem. Res.* 15: 66–72
- Taguchi H, Kunieda N, Kinoshita M 1983 *Makromol. Chem.* 184: 925–933
- Tundo P, Venturello P, Angeletti E 1983 *J. Chem. Soc. Perkin Trans. II* 4: 485–492, 493–496
- Vasudevan T V, Sharma M M 1984 *Ind. Eng. Chem. Process Des. Dev.* 23: 400–406
- Wadekar V V, Sharma M M 1981 *J. Sep. Process Technol.* 2: 1–15
- Woodruff H B 1983 *Proc. of fifth Symp. on biotechnology for fuels and chemicals, biotechnology and bioengineering symposium No. 13* (New York: John Wiley)
- Yadav G D 1975 *Chem. Ind. Dev.* 9: 16–23
- Yadav G D, Sharma M M 1981 *Ind. Eng. Chem. Process Des. Dev.* 20: 385–390