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INTENSIFICATION OF HETEROGENEOUS REACTIONS : THEORY AND PRACTICE

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Heterogeneous reactions are of great industrial, biological, physiological and ecological importance. There is great scope for new investigations with the idea of further intensifying these reactions and making them more selective. Illustrative examples are given to show how the basic theory can help immensely in arriving at rational procedures for the design of reactors and resolving several paradoxes.

Gas-liquid reactions can benefit by deliberate addition of an immiscible liquid phase which exhibits substantially higher solubility. Operation under supercritical conditions may bring out new desirable features. Reactions in macromolecular media can exhibit unexpected behaviour.

Intensification of liquid-liquid reactions can be approached in several ways and the use of phase transfer catalysis, micellar catalysis, hydrotropic agents, microemulsions, etc. stand out as very practical methods and industrially important examples will be given.

Reactions can be deployed to carry out difficult separations which are otherwise not possible or practicable by physical methods involving distillation, extraction, crystallization, etc. Here, new regenerative methods may be possible.

Intensification of solid-liquid reactions has hardly received the attention it merits and some areas will be delineated.

Three phase reactors can show novel and highly desirable features when solid particles are smaller than the diffusion film thickness and some case studies will be shown. It is necessary to re-examine models for emulsion and slurry polymerisation reactors. Fixed bed reactors may show peculiar behaviour with changing liquid loads.

New or modified strategies for design can help immensely and simulation of large size reactors can be very rewarding.

New designs of reactors need to be considered.

Key Words : Heterogeneons Reactions; Design of Reactors; Gas-Liquid, Liquid-Liquid, and Solid-Liquid Reactions; Phase Transfer and Micellar Catalyses; Hydrotropic Agents; Microemulsions

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Note : The Lecture was delivered at INSA, New Delhi.

I am indeed honoured to have been invited to give this prestigious lecture of the Academy and would like to express my most sincere appreciation.

It was thoughtful of Dr P B Sarkar to have made an endowment in the Academy for the purpose of rewarding someone who has made use of scientific work for realising practical results. My predecessors Dr Sukh Dev and Dr Nitya Anand are very talented and gifted chemists who have made innumerable contributions. I wonder whether I really deserve the honour bestowed on me and in all humility accept it with great pleasure.

My own research work over last twenty five years has been in the area of heterogeneous reactions and reactors. In 1964 when I joined the University Department of Chemical Technology, I had hardly any grant for research work (not even Rs. 10,000 per year !) and I had to plan research work which was heavily idea-oriented. I thought it desirable to take up work in heterogeneous reactions involving gas-liquid, liquid-liquid and three phase reactions with a view to understand interaction between diffusion and kinetics of fast reactions and with a fond hope of finding clues to intensify such reactions. I thought that this area would also be intellectually satisfying.

Heterogeneous reactions are of great industrial, biological, physiological and ecological importance. Industrially important reactions are predominantly heterogeneous. There are many instances in practice where a chemical reaction is deliberately imposed and the system made heterogeneous to achieve certain objectives associated with the selectivity of reaction, improvement in yield, adoption of milder operating conditions, achieving the desired degree of removal/recovery etc. A wide variety of situations are encountered in practice where the level of production may be on few hundred to few thousand tonnes/day scale down to production of fine chemicals at a level of few tonnes per annum. Further, the extent of reaction or the degree of removal may approach close to cent per cent level.[1]

Table I shows the variety of reactions that we encounter in practice. The solid catalysed reactions, carried out in fixed or fluidised bed reactors, are quite common in practice. The porous catalysts employed in practice invariably offer enormous area in the range of 100 to 1000m^2/g; some low porosity catalysts offer area around 4 to 10m^2/g. Thus, even if a small per cent of the above area is effective then the throughput per unit weight of the catalyst can be enormous. This is the principal reason, apart from a convenient way of conducting a reaction, for the high popularity of adopting this mode of reaction in the vapour phase where a solid catalyst is used in pelleted or powdered form. Sometimes, we have, under actual operating conditions in practice, the catalyst in the melt form dispersed in the porous matrix of the catalyst.

A large number of industrially important heterogeneous reactions involve at least one liquid phase. There are innumerable situations where a single gas or liquid phase reaction is deliberately converted into a multiphase system. Heterogeneous reactions are also exploited for separations. My own research interests have been in this area and therefore, my presentation will be concerned with this class of

TABLE I

Some examples of heterogeneous reactions encountered in practice

System	*Type of equipment normally used*
Absorption of CO_2, COS, H_2S etc. in aqueous solutions of alkalies and amines	Packed and plate columns
Absorption of CO_2 in ammoniated brine in Solvay-type process for soda-ash manufacture	Sectionalised bubble column
Absorption of NH_3 in aqueous acid solutions	Mechanically agitated contactor, spray column
Absorption of nitrous gases in water for nitric acid manufacture	Plate column, packed column
Liquid phase air oxidation of organic compounds	Agitated reactor, bubble column
Hydration of propylene with sulphuric acid to produce isopropanol	Bubble column, packed column
Nitration of aromatic compounds	Agitated contactor, pipeline or coil reactor
Alkylation of organic compouds	Agitated contactor, bubble column, tubular reactor
Conversion of alkenes to alcohols *via* extraction in sulphuric acid	Agitated contactor, pipeline contactor
Manufacture of oximes from ketones using aqueous solution of hydroxylamine sulphate.	Multistage agitated contactor, vibrating plate column extractor
Alkaline hydrolysis of solid esters	Mechanically agitated contactor
Hydrogenation of unsaturated fats using Raney nickel catalyst	Slurry reactor
Hydrogenation of nitro compounds using Pd- or Pt-based catalysts	Slurry reactor
Fischer-Tropsch synthesis : conversion of $CO+H_2$ to CH_4, paraffins, etc. using Ni-MgO catalyst	Slurry reactor
Air oxidation of ethanol to acetic acid using Pd-based catalyst	Trickle-bed reactor
Hydrodesulphurisation and hydrocracking of petroleum fractions using Mo- and W-based catalyst	Trickle-bed reactor
Alkylation of benzene with propylene using phosphoric acid based catalyst	Trickle bed reactor
Conversion of propylene to isopropanol using tungstic oxide based catalyst	Trickle bed reactor
Steam reforming of naphtha	Fixed bed reactor
Catalytic reforming of naphtha	Fixed bed reactor
Catalytic cracking of heavier petroleum fractions	Fluidized bed reactor
Ammonia synthesis	Fixed bed reactor with internal heat exchange
SO_2 oxidation to SO_3 in sulphuric acid production using V_2O_5 catalyst	Fixed bed reactor
Oxidation of ammonia in nitric acid production using Pt-Rh catalyst.	Fixed bed reactor

reactions. We have found this area to be academically exciting and challenging and yet of great mundane value.

We need an intimate knowledge of chemical kinetics, thermodynamics and fluid mechanics to deal with this subject. The vital question to answer is: How do the factors affecting diffusion and chemical reaction influence the rate of reaction, selectivity, degree of reaction etc. ? Table II gives the gamut of problems with which we are concerned in practice. Depending on the relative values of mass transfer per unit interfacial area (referred to as the specific rate of mass transfer) and rates of reactions, we can have markedly different dependence on the operating parameters. Indeed the differences between the apparent and intrinsic kinetics can be dramatically different and unsuspected results may be obtained.

TABLE II

Mass transfer with chemical reaction : different cases

1.	Mass transfer accompanied by an irreversible reaction of general order.
2.	Mass transfer accompanied by a reversible reaction of general order.
3.	Mass transfer in a medium containing more than one reactant.
4.	Mass transfer accompanied by a consecutive reaction : Role of mass transfer factors.
5.	Simultaneous mass transfer of two solutes accompanied by chemical reaction.
6.	Mass transfer accompanied by complicated reactions.
7.	Simultaneous absorption/desorption with reaction.
8.	Gas absorption in a slurry containing sparingly soluble fine particles.
9.	Gas absorption accompanied by reaction catalysed by solid particles (slurry reactors and trickle bed reactors).

It is common to find that the solute undergoing reaction has limited solubility in the phase in which the reaction occurs (often the reaction occurs only in one phase; there are some situations where the reaction occurs in the gas as well as the liquid phase or two liquid phases). Thus we can have first order or pseudo-first order reactions with half-life varying from a few seconds to a millisecond (even approaching millionth of a second) and yet the throughput per unit volume of the reactor is low due to low values of interfacial concentration of the solute. We are greatly concerned with the throughput per unit volume of reactors for economic reasons and we are always on the look out for ways and means of enhancing rates.

It is a fallacy to believe that all industrially important reactions are first order with respect to the solute; there are many situations in practice where the reaction could be zero or second order in the solute. We also encounter complex reaction schemes involving reversible, consecutive, consecutive-parallel reactions, etc. (Table II).

Let us consider the simple case of an irreversible reaction between solute A (gaseous or liquid) and dissolved reactant B which is mth order in A and nth order in B. Table III gives details pertaining to different well-defined controlling regimes. It is clear from Table III that the functional dependence of the

specific rate of mass transfer with respect to [A], [B] and hydrodynamic factors can be vastly different. Consider an interesting and practically relevant example of absorption of lean CO_2 in aqueous solutions of alkanolamines. Depending on circumstances, the observed rate, under industrially relevant conditions, may vary directly with the partial pressure of the solute gas and square root of the concentration of the dissolved species. Under somewhat different conditions the observed rate can become independent of the partial pressure of the gas and directly dependent on the concentration of the dissolved reactive species. A reaction which is intrinsically zero order in the solute can show apparent zero or half-order kinetics. The situation becomes more complicated as we move on to complex reactions.

A variety of cases have been considered but we will cover a couple of examples.

TABLE III

Functional dependence of rate upon $[A^*]$, $[B_0]$ *and hydrodynamics in different regimes*

Regime	*Effect of*:	$[A^*]$	$[B_0]$	k_L
Very slow reactions		$\alpha[A^*]^m$	$\alpha[B_0]^n$	none
Slow reactions		$\alpha[A^*]$	none	αk_L
Fast reactions		$\alpha[A^*]^{(m+1)/2}$	$\alpha[B_0]^{n/2}$	none
Instantaneous reactions		none	$\alpha[B_0]$	αk_L

Intrinsic reaction m^{th} order in **A** and n^{th} order in **B**.

ABSORPTION OF CO_2 AND COS

Theoretical considerations predict that under conditions of practical relevance the specific rate of mass transfer will vary with the square root of the rate constant. Thus, by suitably selecting the amine reactant we should benefit immensely. Indeed a move from aqueous ammonia to monoethanolamine can result in a four-fold increase in the specific rate and hence a corresponding reduction in the reactor volume. A similar argument holds for COS.

We can point out similar examples pertaining to absorption of lean phosphine.

ABSORPTION OF CHLORINE IN AQUEOUS CONCENTRATED ALKALINE SOLUTIONS : DESORPTION OF HClO

This is a case of an exceedingly fast reaction with complicated kinetics involving a volatile product. The problem posed to us was how best the hypochlorous acid (HClO) can be desorbed. Fig. 1 shows typical concentration profiles. We have analysed this problem and shown that contactors which offer high values of gas side mass transfer coefficient and low values of liquid side mass transfer coefficient, such as a spray column, give higher yields of HClO. Thus, the paradox of desorbing HClO at a high rate even though a large excess of caustic soda is present, has

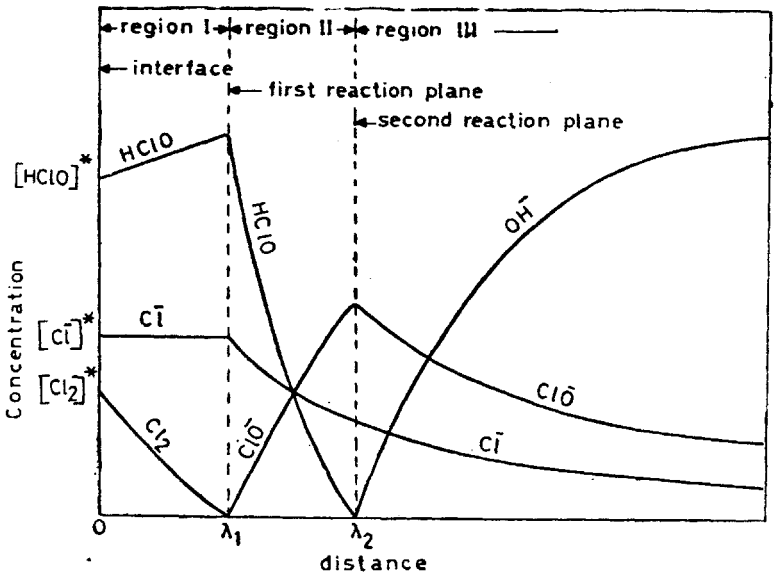


FIG 1 Concentration profiles for absorption of chlorine in aqueous concentrated alkaline solution: Desorption of HClO (Liquid-film resistance-controlled operation)

been resolved and useful tips provided for industrial exploitation.[2] Table IV gives some details. For a more detailed mathematical analysis the reader is referred to the original paper.

TABLE IV

Absorption of chlorine in aqueous concentrated alkaline solutions: desorption of HClO

Partial pressure of Cl_2 at inlet atm	Partial pressure of HClO at outlet atm	$k_G \times 10^5$ mol/cm² s atm	$k_L \times 10^3$ cm/s	Temperature °C	Rate (predicted) $\times 10^6$ mol/cm² s	Rate (observed) $\times 10^6$ mol/cm² s	Yield of HClO
0.544	0.0607	8.122	3.236	75	1.108	1.156	17.9
0.533	0.132	28.0	3.236	75	3.038	2.591	37.0
0.635	0.153	24.41	4.57	55	1.224	1.807	16.94
0.637	0.104	24.41	1.72	55	1.690	1.704	32.54
0.534	0.172	28.0	4.395	75	2.564	2.941	30.60
0.544	0.110	28.0	2.086	75	2.387	2.084	46.0

[NaOH] = 10.2×10^{-3} mol/cm³

All predictions based on equilibrium dissociation

NEW APPROACHES

As indicated earlier, in a large number of cases of practical relevance, the solubility of the solute gas in the medium where the reaction occurs is rather low. We are

also aware of the high interfacial areas that can be realised in liquid-liquid systems in view of lower values of interfacial tension and small differences in the density of the two phases. There are many situations in practice where we can conceive that another immiscible liquid phase may exhibit very high solubility. Consider the case of absorption of C_4 olefins in aqueous solutions of sulphuric acid, where the value of Henry's constant is expected to be below 1×10^{-6} gmole/(cm^3 atm). However, the value of Henry's constant in a medium like chlorobenzene, immiscible in water, will be around 2 to 3×10^{-3} gmole/cm^3 atm. Thus, there is an enormous difference. We can then deliberately employ chlorobenzene, say at 5 to 20 per cent by volume, with or without emulsification, and hopefully obtain higher specific rates of absorption. Recent work from our laboratory in well-designed laboratory experiments has clearly demonstrated the applicability of this innovative idea. In the case of isobutylene and butene-1 values of enhancement factor have been found to be in the range of 8 to 25 with emulsified chlorobenzene. This is truly remarkable. An important point to appreciate is that when the second phase is emulsified, the emulsified droplet is expected to be in submicron to few microns size and thus be smaller than the diffusion film thickness. In such cases the extra flux of the solute gas gets limited by the mass transfer of dissolved solute from the aqueous phase to the emulsified drops and the following differential equation holds :

$$D_A \frac{d^2[A]}{dx^2} = (1 - l_0) k_1 [A] + l_0 k_{LL} a_L ([A] - [A_{L_0}]/m_A) \quad \ldots(1)$$

Boundary conditions are

$$x = 0; [A] = [A^*] \quad \ldots(2)$$

$$x = \delta; [A] = 0, \frac{d[A]}{dx} = 0 \quad \ldots(3)$$

By following the established procedure the following equation for the specific rate of mass transfer is obtained:

$$R_A = K \sinh \left\{ \cosh^{-1} \left(\frac{[A^*]}{K} - 1 \right) \right\} \times \sqrt{D_A((1 - l_0) k_1 + l_0 k_{LL} a_L)} \quad \ldots(4)$$

$$\phi_A = R_A/([A^*] \times \sqrt{D_A k_1}) \quad \ldots(5)$$

$$= \sinh (\cosh^{-1}([A^*]/K - 1))/([A^*]/K)\sqrt{(1 - l_0) + l_0 k_{LL} a_L/k_1},$$

where $K = [A_L] l_0 k_{LL} a_L/((1 - l_0) k_1 + l_0 k_{LL} a_L)$.

In somewhat complicated situations, for accurate results, a more general form of the differential equations for unsteady state conditions is as follows:

$$D_A \frac{\partial^2[A]}{\partial x^2} = \frac{\partial[A]}{\partial t} + (1 - l_0) k_1 [A] + l_0 k_{LL} a_L ([A] - [A_{L_0}]/m_A) \quad \ldots(6)$$

$$\frac{\partial[A_{L_0}]}{\partial t} = k_{LL} a_L ([A] - [A_{L_0}]/m_A) \quad \ldots(7)$$

Initial and boundary conditions are :

$$t = 0,\ x \geqslant 0;\ [A] = 0;\ [A_{L_0}] = 0 \qquad \ldots(8)$$

$$t > 0,\ x = 0;\ [A] = [A]^{*} \qquad \ldots(9)$$

$$t > 0,\ x \to \infty;\ [A] = 0 \qquad \ldots(10)$$

Solutions for the unsteady state partial differential equations can be obtained numerically.

Our experimental data do correlate well with predictions based on equations 4.[3]

It would be appropriate to highlight that the use of artificial blood, where fluorocarbons which exhibit relatively high solubility for oxygen compared to water are employed, makes use of a somewhat similar principle.

Operation under Supercritical Conditions

The operation of gas-liquid reactions under supercritical conditions with respect to the solute (and sometimes also with respect to the phase in which the reaction normally occurs) presents an interesting and potentially useful way of intensifying gas-liquid reactions. Consider the case of propylene as a solute (T_c = 365 °K; P_c = 46 atm). Here, pressures and temperatures above critical values are quite reasonable and we can expect substantial increase in the rates of reaction with an increase in pressure (well above that would be expected on predictions based on Henry's law). Experimental data have yet to be obtained to check the validity of the above proposition.

An intriguing situation can arise in the liquid phase oxidation of isobutane. By operating this reaction, say, in a pipeline reactor at a temperature and pressure of 165 °C and 91atm, respectively, we will work under supercritical conditions. Here, state of the liquid phase will be different from that prevalent in the conventional mode of operation. We may well get higher throughput and better selectivity. Claims have been made in the recent past about the efficacy of the above approach.[4]

Reactions in Macromolecular Media

The manufacture of polyester fibres, films and resins involves desorption of ethylene glycol and we have an interesting situation of desorption preceded by reaction in the diffusion film. Many attempts have been made to correlate experimental and plant data with theory and a considerable success has been seen. An intriguing and unsuspected part came out of simulation of industrial reactors. The desorption of volatile byproducts like acetaldehyde can lead to a substantial improvement in the rate of polymerisation due to higher rates of desorption of ethylene glycol. It is possible to conceive addition of some substances like organoboronic anhydride, diphenyl dicarboxylate, or diphenyl carbonate to augment this vital reaction.

There is, of late, a lot of interest in the hydrogenation of dissolved polymeric substances to eliminate or reduce the level of unsaturation. Homogeneous and

heterogeneous catalysts have been tried. An analysis of this type of reaction system has yet to be made although commercialisation, at least to a limited extent, has taken place. New methodologies of intensifying such reactions need to be developed.

INTENSIFICATION OF LIQUID-LIQUID REACTIONS

Phase Transfer Catalysis

There is a lot of activity in this area for more than a decade and exploitation for industrial purposes has been fairly quick. The utility of phase transfer catalysts (PTC) has been seen in a spectacular way but mostly for reactions free from diffusional limitations. We have shown how mass transfer limited reactions including those where the reaction is sufficiently fast to manifest itself in the diffusion film and may have half-life well below 0.1sec, can benefit by using PTC. Our experiments with alkaline hydrolysis of higher alkyl formates have amply demonstrated the utility of this idea and enhancement factors as high as 250 have been realised. Even for impurity removal like COS from liquefied petroleum fractions, we have shown an enhancement factor of 50.[5] These researches are of considerable value in industry as the size of the reactor can be drastically reduced and this becomes all the more useful when high pressures are encountered (such as in the case of liquefied propylene). A similar strategy may work for the removal of arsine from liquefied C_3/C_4 fractions.

Micellar Catalysis

Micelles are aggregates of surfactants and typically have size of 25–50 Å. Thus, even with a volume fraction of 0.2 to 0.5 per cent, we have a very large number of micelles in the phase where these exist. A lot of work has been reported in homogeneous systems. We argued that in liquid-liquid and solid-liquid systems, with or without mass transfer resistance, we should benefit as the sparingly soluble solute will have very high distribution coefficient in favour of the micellar phase. We have now established, with carefully selected solid-liquid and liquid-liquid systems, even where mass transfer is accompanied by reaction in the diffusion film, that specific rates of mass transfer can be increased by a factor of 5 to 60. In the case of oximation of cyclododecanone, where both solid-liquid and liquid-liquid modes of reactions could be conveniently studied, enhancement factors of upto 60 have been observed.[6]

The following differential equation holds for a typical reaction which is first order in the solute as well as the dissolved reactant species :

$$D_A \frac{d^2[A_w]}{dx^2} = l_m k_{2m} m_A [A_w] m_B [B_{w_0}] + k_{2w} [A_w][B_{w_0}] \quad ...(11)$$

at $$x = 0, [A_w] = [A_w^*] \quad ...(12)$$

$$x = \delta, [A_w] = 0 \quad ...(13)$$

By following established procedures, we obtain the following equation:

$$R_A = k_L [A_w^*] \sqrt{M}/\tanh(\sqrt{M}), \quad ...(14)$$

where
$$\sqrt{M} = (D_A(k_{2w} + l_m k_{2m} m_A m_B)[B_{w_0}])^{1/2}/k_L \quad ...(15)$$
$$= (\sqrt{D_A(k_w + k_m)})/k_L.$$

Our data correlate well with the equations obtained from the above simple model. This strategy of micellar catalysis is commercially attractive.

A unique feature of micellar 'catalysis' is that by appropriate selection of a surfactant, the dissolved ionic species can be repelled and thus we may well be in a position to inhibit undesirable reactions.

It would be useful to explore reverse micelles to intensify liquid-liquid reactions. This will open-up a new strategy for intensifying reactions.

Use of Hydrotropic Agents

We are very familiar with the phenomenon of salting-out of sparingly soluble solutes with electrolytes. However, salting-in can take place with appropriate materials. Hydrotropes are substances which allow large increases in solubility and have been used industrially with detergents, in pigment printing, etc. The uses of hydrotropic agents to increase solubility limited multiphase reactions has hardly received any attention not withstanding the potential this strategy holds. Our recent work brings out this potential. With hydrotropic agents like sodium or potassium salt of toluene sulphonic acid, xylene sulphonic acid, cumene sulphonic acid; butyl monoglycol sulphate, etc., we have seen enhancement factors as high as 500 with alkaline hydrolysis of phenyl and chlorosubstituted phenyl benzoates. This method of intensifying heterogeneous reactions is somewhat unusual.

The increase in solubility due to hydrotropes has been correlated by the following equation over a fairly wide range of the concentration of the hydrotrope :[7]

$$\log_{10}\left[\frac{A_H}{A_w}\right] = k_s I \quad ...(16)$$

The enhancements in rates of alkaline hydrolysis correlate well with the above equation.

It is desirable to arrive at predictive methods which will allow enhancements in solubility to be calculated so that better hydrotropes can be identified. It would be interesting to explore oil soluble agents which will allow high concentration of water in the organic phase.

Use of Microemulsions

Microemulsions are colloidal dispersions consisting of monodisperse droplets of oil in water or water in oil and typically in the range of 100 to 1000Å in diameter.[8] Unlike micellar systems where we are usually restricted to volume fraction well below 2 per cent and where micelle diameter is around 25–50Å, here we can go to hold-up as high as 30 per cent. Thus, extraordinarily high values of interfacial area

can be realised. Both detergent and detergentless microemulsions have been reported. We can clearly discern the synergetic effect of the surfactant and the other organic material, typically isopropanol, *n*-butanol etc. used at levels generally below 2 to 3 per cent. The individual effects of the surfactant and the alcohol are usually much smaller than when present together.

The work reported in the literature is mostly confined to system free from mass transfer resistance. We have worked with our model system of alkaline hydrolysis of phenyl and substituted phenyl benzoate and brought out the efficacy of this strategy. In the case of alkaline hydrolysis of phenyl benzoate the use of 1.2 per cent (*w*/*v*) sodium lauryl sulphate and upto 4 per cent (*w*/*v*) of *n*-butanol resulted in an enhancement in the specific rate in this solid-liquid system of upto 9; the corresponding values of enhancement factor with only 1.2 per cent sodium lauryl sulphate was 5 and 2 per cent *n*-butanol did not show any significant enhancement in the rate. Independent experiments on solubility in the microemulsion media clearly indicated that the enhancements in the rate of reaction were commensurate with the corresponding increase in the solubility.[9]

This strategy holds considerable promise for industrial exploitation not only for a number of organic reactions but also in metal extraction. Fourre *et al.*[10] have shown that extraction of gallium in the presence of aluminium from alkaline solutions is promoted by a factor of 20 when conditions of microemulsion are established. Recently, acidisation of wells in crude oil production has been shown to be affected by microemulsions.[11] There is a possibility that in some gas-liquid reactions we may benefit with this strategy.

Separations through Reactions

In chemical industry, separation of reaction products is of paramount interest and a major part of capital investment and recurring cost is associated with this activity. The most common methods of separation are based on distillation, extraction absorption, crystallisation, etc. However, we do frequently encounter situations where we get close boiling isomeric or non-isomeric, water soluble or insoluble, acidic or basic substances whose separation by the above established methods is not possible or impracticable. Here, we may be able to exploit the differences in the distribution coefficients and ionisation constants in a two phase system and by using a stoichiometric deficiency of a neutralising agent we may be able to get good separation factors. This method is referred to as 'Dissociation Extraction.'

We have developed new strategies with industrially important systems and arrived at novel procedures for regeneration to cut down the cost of chemicals.[12] Table V gives some typical results. In the case of 2,6-xylenol/*p*-cresol we have been able to use aqueous solutions of methylamine to have a regenerative system.[13] In the case of chlorophenols, we have been able to use aqueous solutions of monoethanolamine for separations; the aqueous extract phase can be carbonated to throw out the chlorophenols and the aqueous solution so obtained can be boiled to drive out CO_2 which can then be recirculated.[14] Similar

TABLE V

Regenerative dissociation extraction

System	*Extractant*	*Separation factor*	*Mode of regeneration*	*Reference*
2,3-dichlorophenol/ 2,6-dichlorophenol in toluene	Aq. monoethanol-amine	3.5–5.7	Secondary solvent (Ethylacetate)	Anwar *et al.*[37]
2,6-xylenol/ *m*-cresol in benzene	Aq. methyl amine	6.5	Distillation	Wadekar and Sharma[13]
o- and *p*-nitro-anilines in xylenes	HCl gas	7.1–40.5	Thermal treatment	Jagirdar and Sharma[38a]
o- and *p*-chloro-anilines in xylene	HCl gas	3.2–6.6	Thermal treatment	Jagirdar and Sharma[38a]
p-chlorophenol/ 2,4-dichlorophenol in xylene	Aq. NH_3	3.2–4.9	Distillation	Wadekar and Sharma[13]
p-chlorophenol/2,4-dichlorophenol in toluene	Aq. monoethanol-amine	2.5–3.0	CO_2 absorption distillation	Gaikar and Sharma[14]

strategies have been arrived at by using HCl gas for separation of close boiling cumidines. The above systems illustrate our strategies in getting neat separations in different systems and yet get enhanced rates of extraction.

The following equation gives the value of the separation factor and published data generally correlate well with this equation:[15]

$$\alpha = \frac{K_B X_A}{K_A X_B} \left\{ \frac{N(\delta + 1) + T\left(\frac{1}{X_B} + \frac{K_A \delta}{K_B X_A}\right)}{N(\delta + 1) + T\left(\frac{K_B}{K_A X_B} + \frac{\delta}{X_A}\right)} \right\} \qquad \ldots(17)$$

where

$$N \approx [A^-] + [B^-], \qquad \ldots(18)$$

$$\delta = [HA]_s/[HB]_s$$

and $$T = [HA]_s + [HB]_s.$$

However, to use equation 17 we need to make some experimental measurements of distribution coefficients. The recent work in connection with water pollution on prediction of distribution coefficients in *n*-octanol-water system proved to be handy to arrive at a predictive method for α in dissociation extraction. We have had a fair measure of success in this area and some typical cases are given in Table VI. This has also enabled us to make predictions about the solvent to be used in practice and some interesting and useful cases are reported in Table VII.

TABLE VI

Prediction of separation factor for dissociation extraction

System	*pKa at 25 °C*	*Solvent (α) Reference*	*Suitable Solvent*	*Separation Factor*
phenol *o*-chlorophenol	10.0 8.48	benzene (1.9–2.4) Laddha and Sharma[39]	Polar solvent	*n*-octanol (5.39–6.8) Gaikar and Sharma[17a]
o-cresol 6-chloro-*o*-cresol	10.3 8.69	benzene (1) Di-*n*-butylether (4–5) Wadekar and Sharma[15a]	Polar solvent	*n*-octanol (8–9.18) Gaikar and Sharma[17a]
2,6-xylenol guaiacol	10.62 9.93	anisole (9.7–9.8) benzene (19.7) Jagirdar and Sharma[38]	Polar solvent	*n*-octanol (42.05) Gaikar and Sharma[17a]
p-cresol guaiacol	10.28 9.93	benzene (0.6–0.7) anisole (0.8–0.9)	Polar solvent	*n*-octanol (6–6.4) Gaikar and Sharma[17a]
o-ethylphenol guaiacol	10.2 9.93	ethylbenzene (8.6) benzene (6.5) Jagirdar and Sharma[38]	Polar solvent	*n*-octanol (23.7) Gaikar and Sharma[17a]

TABLE VII

Selection of solvent for dissociation extraction

System	*pKa* at 25 °C	*Solvent (α) Reference*	*Suitable solvent*	*Separation factor*
1. 2,6-xylenol *m*-cresol	10.62 10.10	benzene (15–22) di-*n*-butyl ether (8–13) Wadekar and Sharma[15a]	Inert solvent	*n*-heptane (46.83)
2. 2,6-xylenol *p*-cresol	10.62 10.28	benzene (9–13) di-*n*-butyl ether Wadekar and Sharma[15a]	Inert solvent	*n*-heptane (27–30)
3. *o*-cumidine *p*-cumidine	4.42 4.87	cumene (4–5) *n*-octanol (1.71) Gaikar and Sharma[14]	Inert solvent	*n*-heptane (6)
4. 2,6-xylidine	3.95	di-*n*-butyl ether (4)	Inert solvent	*n*-heptane (4.8)
2,5-xylidine	4.53	Wadekar and Sharma[13]		Gaikar and Sharma[17a]

We have made further progress in this area by evolving strategies for dissociation leaching (e.g separation of a mixture of *o*- and *p*-chlorobenzoic acid in a solid-liquid system).

We have recently shown that dissociation extraction crystallisation may be feasible for some industrially important reactions. Consider the case of a mixture of 2,6-xylenol and *p*-cresol. *p*-Cresol can be selectively crystallised as a complex with anhydrous piperazine, from the mixture of 2,6-xylenol/*p*-cresol dissolved in a suitable solvent, e.g. *n*-heptane.[16]

There are many other instances where reactions prove to be useful in separations even though mixtures may not consist of acidic or basic compounds and a reference may be made to the recent state-of-the art review by the author on this subject.[12] We are greatly interested in evolving oxygen enrichment processes using regenerative absorbents.

Use of Hydrotropic Agents for Separation

This strategy was indicated more than forty years ago but somehow has not received the attention it deserved. We have taken up this work and have shown how separation of 2,6 xylenol/*p*-cresol, *p*-chlorophenol/2,4 dichlorophenol, etc can be attempted. Consider, once again, the case of 2,6 xylenol/*p*-cresol, dissolved in an organic solvent. When this solution is equilibrated with aqueous solutions of hydrotropes such as, K- and Na-*p*-toluene sulfonate, K- and Na-*p*-xylene sulfonates, *p*-cresol can be preferentially extracted. Thus, we get a clue that rates of dissociation extraction can be further enhanced by employing hydrotropes apart from arriving at a novel procedure for separation of close boiling mixtures.[17]

A remarkable feature of the hydrotropy is that by dilution the solute can be thrown out (see equation 16 which indicates exponential relationship). Thus, we can recover the constituents of a mixture and the diluted solution can be concentrated by evaporation and recycled. Thus by indirect thermal means we are able to realise difficult separations. Alternatively, solvent extraction from the aqueous solution with a polar water immiscible solvent may be possible.

Recovery of Valuable/Toxic Substances from Aqueous Waste Streams

This is a very challenging area as we often encounter toxic highly water soluble substances in aqueous waste streams. Here, the conventional methods of aerobic treatment do not work. Further recovery by simple solvent extraction or adsorption is also not possible.

We have shown that phenolic streams from aqueous alkaline streams can be treated in an imaginative way *via* recovery through a reaction system leading to a valuable product; phase transfer catalysts have to be employed to get acceptable rates of extraction and yields. Thus benzoyl chloride, *p*-toluene sulphonyl chloride etc., dissolved in water immiscible solvents like toluene, xylene, etc, can be used and substances like phenol, chlorophenols, resorcinol, etc. in alkaline solutions can be brought down from 3000 to 5000ppm level to well below 100ppm.[18] Table VIII gives some salient features. Thus, not only we convert a liability into an asset but also adopt a methodology to get enhanced rates of extraction.

TABLE VIII

Recovery of phenolic materials from aqueous alkaline streams

Material	*Organic Reagent used*	*Initial Concentration ppm*	*Final Concentration ppm*	*Recovery %*
phenol	benzoyl chloride	5070	3.8	99.92
phenol	*p*-toluene sulphonyl chloride	5200	2.2	99.96
m-cresol	benzoyl chloride	5140	5.5	99.89
resorcinol	benzoyl chloride (2 mol/mol of resorcinol)	5017	2.4	99.95

Concentration of Aliquat 336 : 0.02×10^{-3} mol/cm^3

We have also considered a difficult situation commonly encountered in dyestuff, drug and pesticide industries where aqueous waste-streams containing aromatic sulphonic acids in the presence of a relatively large excess of sulphuric acid are encountered. It is very difficult to treat such waste-streams and the toxic aromatic sulphonic acid (simple or substituted with nitro, hydroxy, halo groups) poses a serious hazard. We argued that it should be possible to use high molecular weight amines, such as tri-*n*-octylamine, dilaurylamine, etc., dissolved in water immiscible polar solvent like 2-ethyl hexanol, to extract the aromatic sulphonic acid. Our experiments have established the feasibility of this process. It is even more interesting to report the selective extraction of the aromatic sulphonic acid by using stoichiometric deficiency of the amine.[19] Table IX gives some salient details of the above work. Here, by employing an instantaneous reaction we can not only intensify the rates of reaction but also bring down the impurity to an acceptable level. Additionally, the extracted material may well have a monetary value.

TABLE IX

Selective extraction of aromatic sulphonic acids from mixtures of sulphuric and sulphonic acids

Acid	*% Extraction*	*Separation factor*
p-toluene sulphonic acid	82	120
m-nitrobenzene sulphonic acid	80	65

Extractant—Tri-*n*-octylamine used in stoichiometrically deficient quantity (equivalent to the amount of sulphonic acid present);
Solvent—2-ethylhexanol; phase ratio—1 : 1; initial concentration of sulphonic acid–5000ppm;
Weight ratio of sulphuric to sulphonic acid—10 : 1.

INTENSIFICATION OF SOLID-LIQUID REACTIONS

Solid-liquid reactions are of great practical importance and examples range from acidulation of phosphate rock to leaching of ores. In spite of its great practical importance scant attention has been given to this subject particularly with respect to intensifying these reactions.

It is known that solid-liquid reactions, with or without mass transfer resistance, may benefit from the use of dispersing agents which prevent agglomeration of particles. Even in this area we do not have proper guidelines.

We have recently started work in this area with simple but industrially important systems. Consider the case of reaction between sulphur and aqueous caustic soda (temperature > 70 °C) to give sodium sulphide/disulphide. This reaction is influenced by polyethylene glycols, cetyl trimethyl ammonium bromide, etc., and enhancements in rates, under other wise uniform conditions, by a factor as high as 7.5 have been observed. It was somewhat intriguing to find that the enhancement factor goes down substantially with concentrated solutions of sodium hydroxide.[20] There is a mention in early literature[21] that the reaction between sulphur and sodium sulphite to give sodium thiosulphate is amenable to catalysis by dodecyl pyridimum bromide, benzyl pyridinium chloride, etc.

It is also important to realise that by a careful selection of a surface active agent providing a charge which is the same as the dissolved reactive species we can inhibit the reaction as the reactive species will be repelled.

The role of phase transfer catalysis in enhancing a variety of solid-liquid reactions has been brought out even with respect to the classic system of the reaction between benzyl chloride and solid sodium acetate/benzoate to give the corresponding benzyl ester. We have shown a few years ago how by using a proper phase transfer catalyst this reaction can be enhanced by a further factor of at least twenty five compared to the current practice of using triethyl amine, which *in situ* gets converted to benzyl triethyl ammonium chloride and acts as a PTC.[22]

We have pursued these types of reactions in the recent past and have shown how the reaction between benzyl chloride and Na_2S/Na_2S_2 in a solid-liquid system can be greatly accelerated. Here, we could also work with the liquid-liquid mode of operation and hence, appropriate comparison can be made. For solid-liquid system enhancement factors as high as 4000 have been realised.

Solid-liquid reactions may be amenable to intensification through miceller catalysis, microemulsion and hydrotropy. We do have some examples pertaining to systems cited in the text. As reported earlier even the acidisation of rock in oil-well drilling and production may be amenable to changes with microemulsions.[11]

Three Phase Reactions

We commenced our work in this area almost 16 years ago. Our impetus to look into this area came from our contacts with industry and with respect to a seemingly simple but otherwise very complicated system of the carbonation of lime slurry to give precipitated calcium carbonate. Calcium hydroxide is sparingly soluble in water (6 to 7 $\times$ 10^{-5} gion/cm^3) and the reaction between dissolved CO_2 and OH^- has a second order rate constant around 10^7 cm^3/(mol sec). Thus, the reaction between dissolved CO_2 and OH^- occurs in the diffusion film and is complete within a short distance of well under 50 to 100 microns from the gas liquid interface.

In the process of making calcium hydroxide by slaking of quick lime we can, without expenditure of extra energy, obtain particle size below 2 microns. We thus have a unique situation of sparingly soluble fine particles simultaneously dissolving in the diffusion film while the reaction is going on. The following differential equations hold for an instantaneous reaction :[23]

$$D_A \frac{d^2[A]}{dx^2} - k_{SL}a_p \frac{[B_s]}{z} = 0;\ 0 < x < \lambda \qquad ...(19)$$

$$D_B \frac{d^2[B]}{dx^2} + k_{SL}a_p([B_s] - [B]) = 0;\ \lambda < x < \delta \qquad ...(20)$$

Boundary conditions are :

$$x = 0;\ [A] = [\overset{*}{A}] \qquad ...(21)$$

$$x = \lambda;\ [A] = [B] = 0;\ -D_A \frac{d[A]}{dx} = \frac{D_B}{z} \frac{d[B]}{dx} \qquad ...(22)$$

$$x = \delta;\ [B] = [B_s] \qquad ...(23)$$

By following the established procedure we can show that the specific rate of mass transfer is given by :

$$R_A = \frac{[B_s]}{z} \sqrt{D_B k_{SL} a_p} \qquad ...(24)$$

provided that, $\delta \sqrt{k_{SL}a_p/D_B} > 5$ ...(25)

and $[B_s]/z \gg [A^*]$ ...(26)

This is a unique situation as now the rate of gas-liquid reaction varies directly with the square root of particle loading. For a specified loading, the rate varies inversely with the particle size.

When the above work was reported, its implications for flue gas desulphurisation were not realised as this problem had not really become important. Subsequently, the efficacy of our model could also be seen in lean SO_2 removal by slurries of lime or limestone. Thus, rates of reaction are intensified even by an order of magnitude by using the same wt % loading of the slurry but by varying the particle size.

The problem of carbonation of lime slurry continues to attract us as there are many unresolved problems associated with the effect of operating variables, additives, etc., on the particle size distribution and crystal type. The crystal size distribution is of great practical value apart from the crystal habit. A real intriguing part is the prediction of growth rate when the nuclei are simultaneously generated in the diffusion film. Perhaps, this may indicate yet another novel way of intensification.

The role of solid particles which may have high adsorption capacity for the solute or which are catalysts for a reaction which is already sufficiently fast to

occur in the diffusion film has also been recently brought out by us.[24] The following differential equation holds for catalytic particles which enhance reactions which are sufficiently fast to manifest in the diffusion film :

$$D_A \frac{d^2[A]}{dx^2} = k_1[A] + k_{SL}a_p[A] \quad ...(27)$$

$$x = 0;\ [A] = [A^*],\ \frac{d[B]}{dx} = 0 \quad ...(28)$$

$$x = \delta;\ [A] = 0 \quad ...(29)$$

By following the established procedure we can show that the specific rate of absorption is given by

$$R_A = [A^*]\sqrt{D_A k_1 + D_A k_{SL} a_p} \quad ...(30)$$

It is clear from equation that when $D_A k_{SL} a_p \gg D_A k_1$ the effect of solid particles dominates on the value of the intrinsic first order or the pseudo first order rate constant becomes important.

We have checked the above model with the well-known industrially important system of the oxidation of aqueous Na_2S to $Na_2S_2O_3$ catalysed by fine carbon particles at temperatures higher than 70 °C. By carefully selecting operating conditions, which involved working at temperatures as high as 140 °C and therefore higher pressures, we could show how fine catalyst particles can do a marvellous job. In this system we can have very high loading of coarse carbon particles (size greater than diffusion film thickness) and this will not result in any enhancement in the rate as all the oxygen is consumed in the diffusion film. Thus, a unique method of intensifying an already fast reaction has been brought out.

We have been able to use fine carbon particles to 'catalyse' a variety of solid-liquid and liquid-liquid reactions. Here, these particles carry out the function of facilitated transport—pick up solute in the diffusion film and shed it in the bulk phase. We have seen enhancement in rates for mass transfer controlled reactions by a factor of 4 to 5 which is quite remarkable. Thus a new method of facilitated transport has been suggested.

The above examples are illustrative and commercial exploitation will be facilitated by magnetising the fine particles, if these are not magnetic, and then on-line high gradient magnetic separation can be used.

The role of fine particles smaller than diffusion film thickness has probably many more applications and implications than visualised so far. Consider the case of slurry polymerisation of propylene, ethylene etc. with Ziegler-Natta type catalysts. Here the initial particle size of the catalyst can be sub-micron and the polymer grows on the catalyst. As far as we know, this unique feature of growth right in the diffusion film has not been recognised in predicting the final particle size distribution.[1] Similarly, in the case of emulsion polymerisation, the prediction of final latex size distribution should recognise the importance of small sub-micron

to micron size droplets of the monomer at the start of polymerisation. The above features may well bring out hidden variables which, apart from other factors, cause intensification of rates of polymerization.

Three Phase Fixed Bed Reactors

These are very popular in hydrotreating petroleum fractions, manufacture of cumene, etc. A lot of studies have been made in this area with respect to flow regimes, methods of discerning controlling mechanism, scale-up etc. However, there are still some important areas which merit attention. The behaviour of such reactors when one of the phases is supercritical, e.g. in absorption of propylene in water to give isopropanol, merits attention. Further, when two liquid phases are encountered (e.g. in manufacture of isopropanol) the established procedure for characterisation of flow regimes and predicting mass transfer coefficient may need modification. The above situation may lead to considerable intensification.

For volatile liquid phases and for low liquid flow rates which are inadequate to wet the pelleted catalyst we may encounter peculiar behaviour associated with a reduction in global rate with an increase in the liquid flow rate and multiple steady states. These merit further attention.

Use of Ultrasound (US) in Intensifying Multiphase Reactions

A variety of reactions, such as, Pd-catalysed hydrogenations of alkynes and alkenes, reduction of aromatic nitro-compounds to the corresponding anilines, olefin isomerization, zinc catalysed condensation of carbonyl compounds with bromoesters to beta-hydroxy esters, Friedel-Craft acylation of toluene and derivatives to produce ketones, etc. have been 'catalysed' by ultrasonics to varying degrees.*[25] In the case of some hydrogenations 1000-fold increase in rate has been observed, for olefin isomerization 100,000 fold increase has been noted. This area merits further attention particularly mass transfer limited reactions. It appears that the formation of tiny bubbles, and collapse of bubbles, which may well raise local temperatures and pressures markedly, are responsible for the observed behaviour.

Reactions involving Three Liquid Phases

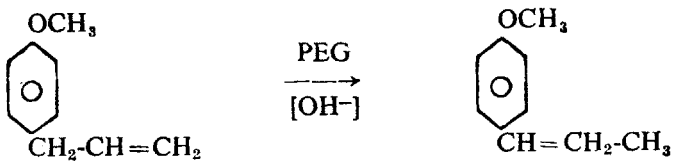
We may encounter three liquid phases as a part of an extraction process or we may deliberately like to create such a situation to achieve certain objectives. For separation of thorium from fission products and from other heavy metals, tri-*n*-butyl phosphate (TBP) dissolved in *n*-dodecane, is used as an extractant. The complex of thorium with TBP has limited solubility in *n*-dodecane and therefore appears as a second organic phase. Leonard *et al.*[26] have demonstrated satisfactory functioning of staged liquid-liquid contactors where three liquid phases are encountered. There is a need for further investigations in this area as both hydrodynamics and mass transfer characteristics are affected by the generation of the third phase.

*See e.g. Suslick *et al.*[25] and references therein.

We have referred to the use of phase transfer catalysts (PTC). Many attempts have been made and are being made to use PTC as solids so that the recovery of the catalyst is greatly facilitated. We have now voluminous literature on this subject, but it is doubtful if any commercial exploitation has been done. As against this backdrop we can conceive situations where the product might come out as a third phase and thus the recycling of PTC becomes relatively easy. Alternatively, the PTC may exist as a third liquid phase.

The oligomerisation of ethylene to higher alpha-olefins can be cited as an example in gas-liquid reaction system, containing homogeneous catalyst in the form of nickel phosphine ligand dissolved in glycol, where the product appears as a second liquid phase.

The recent work of Neumann and Sasson[27] for the following isomerisation reaction :



is very interesting. By using 40 to 50 per cent KOH and polyethylene glycol (PEG) 400 a third liquid phase consisting of KOH-PEG complex is formed and the isomerization reaction can be intensified in a very useful way. This type of strategy may have utility in other areas.

Process Design and Simulation

Process design of gas-liquid, liquid-liquid and three phase reactors has received some attention.[28–31] We will consider some typical examples to bring out the importance of a rational approach.

Semi-Batch Mechanically Agitated Gas-Liquid Reactors

These are very common in practice for halogenation, oxidation, ozonation, etc. We often have a constraint associated with the percentage of solute in the outlet gas due to either safety reasons or health hazards. The designer, therefore, tries to be conservative and so plans that under no circumstances the outlet percentage of the solute gas exceeds the specified limit by basing rates of reactions that are realised towards the tail-end of the operation. Thus, the reactor capacity is not properly exploited. We have analysed this problem and set up a simple model and shown how the batch time can be very substantially reduced by having a proper flow rate of the solute modulated through a controller. Let us consider a case of a mechanically agitated reactor for ozonation with ozonised oxygen or air, of an olefinic compound. This reaction is first order in ozone as well as the olefinic compound and the value of the second order rate constant at the operating temperature is around 10^7 cm^3/(mol sec). The reaction is very fast to occur completely in the diffusion film and the following equation holds.[28]

$$-G\frac{dx}{dh_a} = a\,\mathrm{HPS}\left(\frac{x}{1+x}\right)\sqrt{D_A k_2[B_0]} \qquad \ldots(31)$$

Boundary condition : $h_a = 0;\ x = x_i$ ...(32)

The solution for equation 31 is :

$$(x_i - x_0) + \ln\left(\frac{x_i}{x_0}\right) = \frac{a\,\mathrm{HPV}_a}{G}\sqrt{D_A k_2[B_0]} \qquad \ldots(33)$$

Thus, a useful method of enhancing the capacity of reactors has been brought out.

Air Oxidation of Black Liquor

Air oxidation of dilute and concentrated black liquor in paper plants is widely practised for the conversion of sodium sulphide to sodium thiosulphate at temperatures higher than 70 °C. A variety of contactors such as packed columns of special design, plate columns, bubble columns, pipeline contactors, etc. are used in practice. We have considered this problem and have shown that an optimal design should be based on horizontal sparged reactor rather than the conventional vertical bubble column reactor. Here, the power consumption per unit oxygen consumption is much lower in the case of the horizontol sparged reactor. We also do not have constraints associated with the outlet percentage oxygen as it poses no hazard of any kind and the value should be decided on economic considerations.

The process design of the horizontal sparged reactor can be approached in a systematic way. We can even predict the extent of backmixing in the liquid phase and the scale-up to real large size units can be approached with some confidence.[32,33]

The example is of a different kind to show how intensification in rates can be achieved for the same value of power consumed per unit volume. Further intensification can be realised by using dissolved metal ions like Fe, Cu etc. and activated carbon as catalyst. It so happens in pulp plants that we get metal ions as well as carbon particles which are obtained in the wet burning of the dissolved organics.

Three Phase Reactors : Slurry Reactor for Hydrogenation of Aqueous Ammonium Nitrate to Hydroxylamine in Acid Medium

The manufacture of hydroxylamine salts *via* catalytic hydrogenation of aqueous acidic solutions of ammonium nitrate has acquired considerable importance in practice. Here Pd/Carbon catalyst is used with particle sizes often below 20 microns and the reaction is conducted under pressure of a few atmospheres. First of all, the selectivity with respect to hydroxylamine is partly realised through using fine catalyst particles and deliberately making the process essentially mass transfer controlled. Thus, hydrogen on the catalyst surface is not available to allow over-reduction of hydroxylamine to ammonia. We require reasonably good residence time of liquid to obtain specified levels of conversion. Thus, bubble column reactors or mechanically agitated reactors can be considered. One important

advantage of bubble columns is that we do not have the shaft seal and stability problems but as against this, hydrogen flow rates have to be far in excess of that required stoichiometrically to provide good agitation and to keep solid catalyst particles in suspension. Thus, hydrogen recycle *via* a recycle compressor is a necessity in bubble column reactors.

We have shown how in large size reactors for a specified value of power input per unit volume, we can realise superior mass and heat transfer characteristics in bubble column reactors compared to that in mechanically agitated contactors.[34] This may sound paradoxical but hydrodynamic analysis of bubble columns reveals that liquid circulation velocities can be superior to those in mechanically agitated contactors and height to diameter ratio is unimportant as multiple circulation cells with characteristic dimension roughly equal to the column diameter are created. This is another example to show how for a specified power consumption per unit volume a higher rate can be realised, apart from safer and more reliable operation.

Simulation of Large Size Industrial Reactors

This can be very rewarding and valuable clues may be provided for intensifying the rates to realise higher output from existing assets. This can be illustrated with the example of the manufacture of polyesters and absorption of NO_x.

Polyesters

As indicated elsewhere in the text the crucial stages in the polymerisation involve desorption of glycol as the key step. However, this is hedged by many side reactions which are quantitatively of small importance but otherwise very important. Mashelkar and his co-workers have clearly demonstrated the prowess of simulation in this area where worldwide production exceeds 6 million tones per annum.[35]

Absorption of NO_x in Aqueous Alkaline Solutions : Selectivity with Respect to Nitrite

This is a very interesting example to show how proper simulation can give valuable clues. It can be shown, contrary to expectations, that a rise in temperature, under otherwise uniform conditions can lead to very substantial improvement in selectivity with respect to nitrite apart from an increase in rate. This sounds paradoxical but a number of reactions take place in the gas phase as well (see Fig. 2). Thus, with an increase in temperature, vapour pressure of water rises sharply and the rate of formation of HNO_2 in the gas phase increases and since absorption is accompained by an irreversible reaction in the alkaline medium we do not have problems of equilibrium partial pressures of HNO_2, N_2O_3, N_2O_4, NO_2 over the solution.[36]

Process Intensification through New and Modified Design of Reactors

The flue gas desulphurisation, treatment of wastewater on very large scales, solvent extraction of metals from dilute aqueous solutions, hydroprocessing of heavier petroleum fractions, etc. are real large scale operations which provided

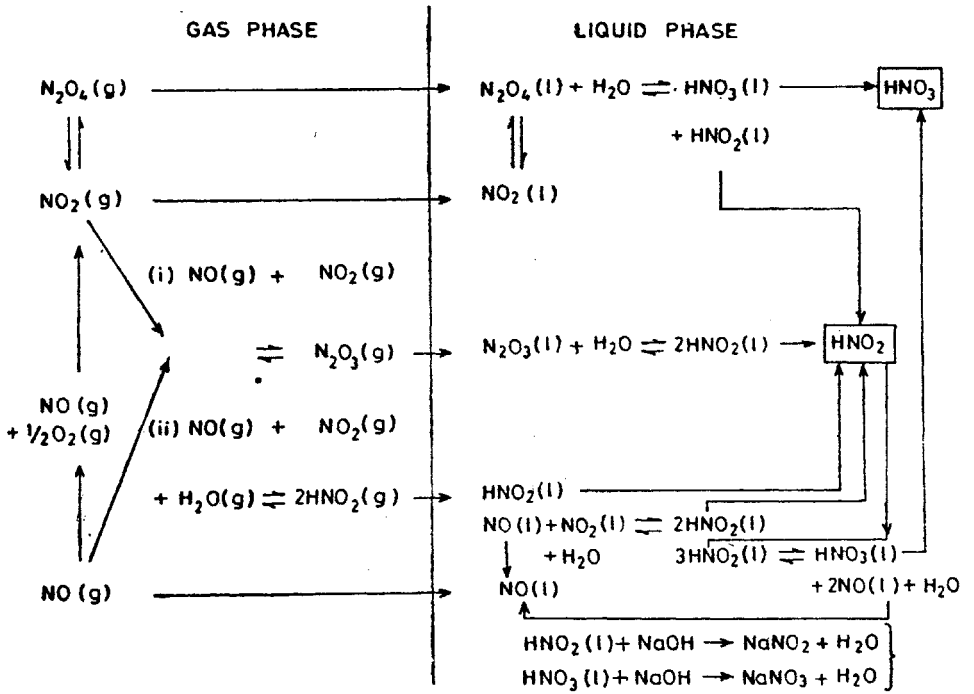


FIG 2 Absorption of nitrous gases

impetus to look into new and modified designs. Consider the case of wastewater treatment having high BOD values and this, in practice, has close parallel with large scale reactors for protein from methanol as a substrate. Here, apart from the need for high values of liquid side mass transfer coefficient we need to have very high water circulation rates to allow high heat transfer coefficients and to keep solid particles suspended. Designs with external as well as internal loops have been developed (*see* Figs. 3 and 4). In the case of fermenters these reactors are kept above ground to allow easy access for cleaning but for wastewater these can be below ground and are, therefore, sometimes referred to as deep shaft aerators and may have a depth of upto 300m.[1] An interesting feature is that absorption of oxygen occurs as liquid flows down and desorption of CO_2 occurs while liquid is ascending—conditions which are favourable for the respective operations.

CONCLUSIONS

The probing of intensification of heterogeneous reactions has been academically and professionally very rewarding. In many cases solutions call for negligible increase in cost but returns are very attractive. There are various approaches to this problem from new basic ideas to making modifications in the existing designs or operating conditions. A variety of examples have indicated the prowess and potential of this area. Every time our approach led to some intensification it emboldened our interest and newer and more daring approaches for intensification were scouted.

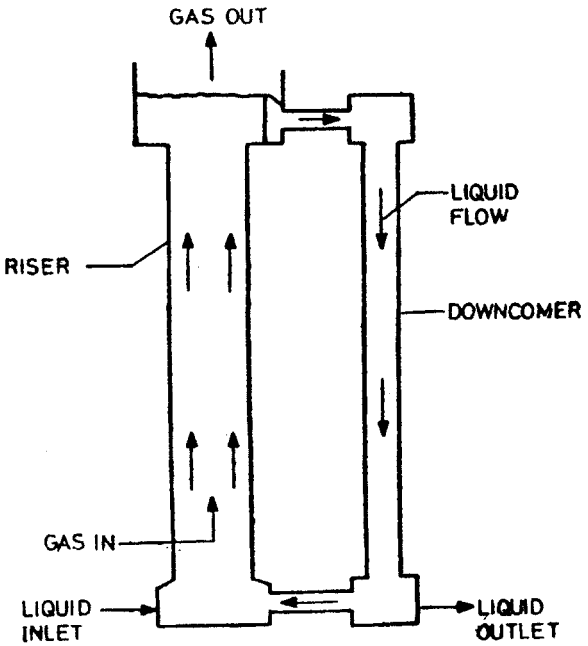


FIG 3 Gas-liquid reactor with external loop.

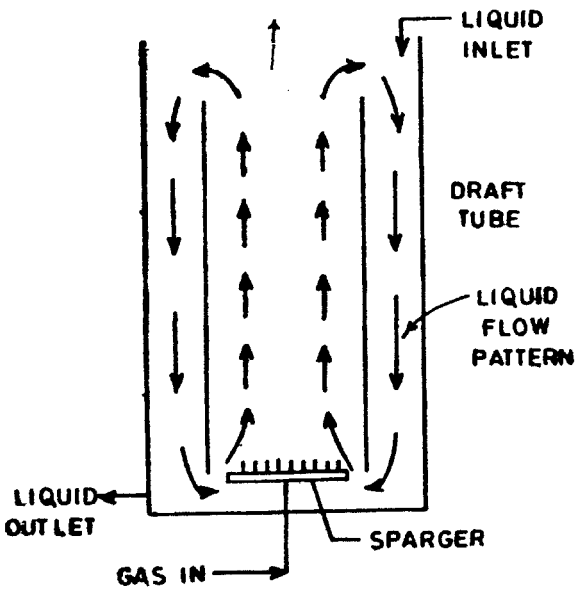


FIG 4 Gas-liquid reactor with internal loop.

NOTATION

$\mathbf{A}$ = gaseous solid, or liquid-phase species that is being transferred from one phase to another.

$[\mathbf{A}]$ = local concentration of A at any point in the B phase, mol/cm³.

$[\overset{*}{\mathbf{A}}]$ = concentration of A at the interface, mol/cm³.

a = gas-liquid or liquid-liquid interfacial area per unit volume of contactor or dispersion, cm²/cm³.

a_L = liquid-liquid interfacial area, cm²/cm³ (organic phase volume).

a_p = solid-solid interfacial area, cm²/cm³ (clear liquid volume).

$[\mathbf{A}_{Lo}]$ = concentration of A in organic droplet, mol/cm³.

$\mathbf{B}$ = dissolved reactive species present in the B phase.

$[\mathbf{B}]$ = local concentration of B at any point in the B phase, mol/cm³.

$[\mathbf{B}_o]$ = concentration of **B** in the bulk **B** phase, mol/cm³.

$[\mathbf{B}_s]$ = concentration of **B** at solid-liquid interface, mol/cm³.

D = diffusion coefficient of the dissolved species as indicated by subscript, cm²/s.

G = gas flow rate, cm³/s.

H = solubility coefficient, mol/cm³ atm.

$[\mathrm{HA}]_s$ = concentration of acids HA and HB, respectively in the organic
$[\mathrm{HB}]_s$ phase, mol/lit.

h_d = dispersion height, cm

I = ionic strength of solution, gion/lit.

k_1 = pseudo-first-order rate constant defined as $k_n\,[\mathbf{B}_o]^n$, s^{-1}.

k_2 = overall second order rate constant, cm³/mol s.

k_n = overall nth order rate constant, $(\mathrm{cm}^3/\mathrm{mol})^{n-1}\,\mathrm{s}^{-1}$.

k_G = true gas-side mass transfer coefficient, mol/cm² s atm.

k_L = true liquid-side mass transfer coefficient, cm/s.

k_{SL} = true solid-liquid mass transfer coefficient, cm/s.

k_{LL} = liquid-liquid mass transfer coefficient for aqueous to organic phase (based on aqueous phase), cm/s.

k_S = Setchenow constant, cm³/mol.

K_A, K_B = dissociation constants of acids HA and HB, respectively, gion/lit.

k_{2m} = second order reaction rate constant in micellar phase, cm^3 mic/mol s.

l_o = fractional hold-up of organic phase.

l_m = fractional micellar phase hold-up.

m_A = distribution coefficient of A between A-rich and B-rich phases.

P = pressure, atm.

P_c = critical pressure, atm.

R_A = specific rate of absorption or extraction or dissolution of species A, mol/cm^2 s.

S = cross-sectional area of the reactor, cm^2.

t = time, s.

T_c = critical tempereture, deg K.

V_d = dispersion volume in the reactor, or on a plate of the plate column, cm^3.

x = distance into B phase from the interface cm; distance along the reactor length, cm; ratio of moles of A to the moles of inerts in gas.

X_A, X_B = distribution coefficient for the undissociated acids HA and HB, respectively, between aqueous and organic phases.

x_i, x_o = ratio of moles of A to the moles of the inerts in gas at inlet of the reactor and outlet of the reactor.

z = stoichiometric coefficient.

α = parameter defined by equation 17.

δ = thickness of diffusion film (liquid) in the film theory of mass transfer, cm.

λ = reaction plane location measured from the interface, cm.

ϕ_A = enhancement factor for species A.

Subscripts

H = property in hydrotropic solution.

w = property in water.

ACKNOWLEDGEMENT

I have had the pleasure and previlege of having very talented and high calibre research students and what I have presented is based on the work carried out over the years by my collaborators. This medal is a tribute to their work.

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