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Organometallic chemistry and catalysis

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The relationship between organometallic chemistry and catalysis is presented from a historical viewpoint. Important modern concepts such as catalytic cycles, catalytic intermediates, etc. that define the framework of research in *homogeneous* catalysis are introduced. The justifications for the use of *metal clusters* rather than mononuclear complexes as models for *heterogeneous* catalytic reactions are mentioned.

With this introductory background, results from the author's laboratory on ruthenium and platinum carbonyl cluster-catalysed reactions are presented. For complex cluster-catalysed homogeneous reactions, where detailed kinetic studies are extremely difficult to carry out, the usefulness of model building with well characterized reaction steps is shown. Two reactions, reductive carbonylation of nitrobenzene and transfer hydrogenation of cyclohexenone, are discussed in this context. Finally the use of an anion exchange resin as a support material to generate *heterogenized* cluster-catalysts of novel catalytic activities is discussed.

Instabilities at reacting interfaces in ceramic systems

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Nonequilibrium heterogeneous systems are frequently encountered in modern ceramics. The interfaces between adjacent phases move during the course of solid state reaction. In binary systems the interface is invariant under isothermal and isobaric conditions. However, in higher order systems the interface is not invariant. Morphological instability of an initially planar interface becomes feasible. Some experimental observations of instability are presented. Although interface energies tend to stabilize moving planar interfaces, this effect is small when the structures of adjacent phases are closely related. In the absence of a simple general principle that can predict morphological instability, the phenomena can be analysed by transport equations of irreversible thermodynamics under appropriate boundary conditions. A parameter can be defined which can distinguish between stable and unstable interfaces. The parameter determines whether or not small perturbations of the interface will grow or decay with time. The parameter is a complex function of all the transport coefficients, starting compositions and chemical potentials of all components in both phases. Because of the complexity of the mathematics involved and the dearth of necessary input data, the search for a more general principle continues.

A set of important boundary conditions at reacting interfaces correspond to the availability of oxide components and oxygen. They determine the degree of flux coupling in ternary and higher-order systems. When oxygen is excluded from one or more interfaces of a ternary compound, oxygen potential gradients develop as a consequence of cationic fluxes. Oxygen pressures of several hundred atmospheres can develop in the interior of reacting systems, giving rise to pore formation and mechanical deterioration of the ceramic.

Intelligent engineering systems

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Intelligent engineering systems represent evolving new generation engineering systems with embedded computer systems whose performance is enhanced by incorporating several levels of human experience, intelligence, expertise and knowledge. Such systems may be characterized by the presence of several of the following attributes:

—They have ability to pursue goals that evolve with time.

—They have ability to capture, store, use and maintain knowledge from diverse sources.

—They are capable of performing intelligence computations, such as those associated with human

intelligence involving large numerical and symbolic computations for purposes such as problem solving, reasoning, understanding and learning.

—They are composed of a distributed set of interacting intelligent or conventional subsystems.

—They interact intelligently and intelligibly with human users and other such systems.

—They are adaptive in nature, capable of learning from experience, and capable of allocating their own resources and levels of attention to tasks they perform.

While such systems are clearly futuristic, the present-day revolution in computer technology, artificial intelligence and knowledge-based expert systems holds the promise of supplying solutions to major problems in government and industry in the form of intelligent engineering systems.

Such systems are designed using intelligent computer-aided engineering (ICAE), the goal of which is to construct computer programs that capture a significant portion of an engineer's knowledge, both formal and tacit. Issues that are important are ICAE in design, ICAE in plant operation and maintenance, ICAE in computer-based training, and general ICAE methodology, including progress in areas such as qualitative physics and better understanding of human reasoning.

We shall illustrate the underlying principles of intelligent system design with examples drawn from several projects that are in progress in our Intelligent Systems Laboratory, such as the development of a knowledge-based assistant for natural language requirement analysis, a decision support system for project management, development of a design environment for complex pattern recognition tasks, and development of intelligent subsystems for defence applications.

Some novel one- and two-dimensional methods in high-resolution NMR spectroscopy

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With the advent of pulsed Fourier transform NMR spectroscopy many new pulse sequences are being developed to unravel complicated high-resolution NMR spectra of large molecules. In homonuclear systems (such as in ^1H NMR) one can use coherence transfer between coupled protons via spin–spin coupling or rotating frame to generate two-dimensional correlation spectroscopy. The present lecture will cover the basic aspects of coherence transfer and principles of 2D spectroscopy and introduce two novel methods of spectral simplification. In one, homonuclear coherence transfer in the rotating frame is used to generate a simplified subspectrum from a more complicated spectrum. In another, homonuclear coherence transfer is used for the 'preparation' and 'mixing' in a two-dimensional pure zero-quantum a pure double quantum correlation spectroscopy useful in studying amide proton–proton connectivities in proteins in 95% aqueous (H_2O) solutions. The above techniques are demonstrated by suitable examples.

Pressure–temperature–time trajectory of granulites from Ganguvarpatti, South India, and its implications on crustal evolution

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The granulites of Ganguvarpatti, which constitute a portion of the Archaean South Indian belt, include silica-deficient sapphirine-bearing granulites, charnockites, khondalites, gneisses, leptynites and mafic granulites. Numerous interesting reaction textures and coronas including symplectites are well preserved in these granulites. These reaction textures are formed in response to a drop in pressure during uplift. The frozen-in textural and chemical data are suggestive of low μ H_2O, and coexistence of reactants and products in all rocks suggests that chemical potentials of components were buffered by mineral assemblages.

These arrested reaction textures, which preserve the signature of the different stages of metamorphic crystallization, when combined with the pertinent models of geothermobarometry indicate a nearly isothermal decompressive P–T–t trajectory and a fairly rapid uplift of *ca* 15 km. The maximum pressure of 9 kb during the thermal peak indicate *ca* 30 km depth of burial during late Archaean. Considering the average thickness of *ca* 35 km of the preserved crust in the southern Indian Shield, the crustal thickening of Archaean crust (*ca* 65 km) can be explained through the northward subduction during collision and tectonic setting.

Although several other mechanisms are possible

for generating the thickened crust, the clockwise P–T–t loops are more likely a consequence of concurrent thermal relaxation and erosion following tectonic crustal thickening in collision belts.

The characteristic swing in the structural trends at the Moyar–Bhavani lineament and the development of the high-grade assemblages suggest that it is a suture zone along which the indentation of Dharwar craton took place. It remains to be seen whether these rocks suggesting hot uplift necessarily means that they formed in single-cycle collisional tectonic setting or there was an Archaean isobaric cooling phase followed by reheating and uplift at a much later time.

X-ray spectroscopic studies of complex oxides

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X-ray absorption studies of complex systems containing more than one phase and/or more than one type of coordination have been of recent interest to researchers dealing with catalytic materials, amorphous systems and complex oxides. Procedures to extract structural information and application of X-ray absorption spectroscopy (X-ray absorption near edge structure, XANES, as well as extended X-ray absorption fine structure, EXAFS) to the study of such materials will be illustrated by taking examples of simple oxides like CuO, NiO and related complex systems. Typical complex systems, such as $NiAl_2O_4$, containing more than one type of coordination around the metal ion, as well as the applicability of modified EXAFS function to mixed-phase oxide catalysts Cu/ZnO, Ni/Al_2O_3 and Ni/TiO_2 will be presented.

Siting, energetics and mobility of adsorbates in zeolites

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Zeolites are aluminosilicates with complicated three-dimensional structure consisting of interlinked cages and channels. The inner walls of the cages provide a heterogeneous surface where the molecules are adsorbed and reactions occur, resulting in the well-known catalytic properties of zeolites. The size and shape of the cages, channels and windows are responsible for their shape-selective properties. Extensive experimental investigations, including calorimetric, uptake, IR, Raman, NMR, X-ray, neutron scattering, etc., of organic molecules sorbed in zeolites exist in the literature. However, it is only in recent years that attempts have been made at understanding these interesting systems theoretically.

Molecular dynamics calculations have been carried out on rare gases and small molecules adsorbed in zeolites such as faujasite. Concentration and temperature dependence of the adsorption properties have been investigated. Radial distribution functions, adsorbate–zeolite interaction energy distribution functions, site and cage residence times, diffusion coefficients, cage occupancy, diffusion pathways for cage–cage migration and vibration frequencies have been obtained. It is seen that the adsorbates are rarely found near the centre of the cage. Site-to-site migration of methane in faujasite begins around 150 K. Below this temperature the methanes are localized to the region near the adsorption site. For benzene there are two adsorption sites—the cation and the window site. The motion of the adsorbate in general is highly anisotropic. The calculated vibrational frequencies are in good agreement with neutron scattering data wherever available, and with the grand canonical ensemble Monte Carlo calculation of Rowlinson and coworkers.

Novel aspects of quantum theory of magnetism

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There has been a renewed interest in the quantum theory of magnetism of insulators following the discovery of high-temperature superconductivity in doped antiferromagnetic insulators. Fascinating connections of some of the problems of magnetism have been made to rather unexpected and parallel developments in fractional quantized Hall effect in condensed matter physics, topological field theory in quantum field theory, and theory of knot polynomials in pure mathematics. I will present some older examples of this phenomenon of parallel developments and argue that historically this is not new. Two specific cases will be discussed at some length. The first one is the phenomenon of pairing and superfluidity occurring in superconductors and ^3He superfluids—this has its parallel in magnetic insulators. Secondly I will discuss how the aforementioned recent parallel developments can be understood in a

unified way through the notion of dynamically generated gauge fields in the study of strongly correlated systems introduced by Anderson and the present author.

The physics of fluctuating membranes

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From the point of view of a physicist, a membrane is a two-dimensional sheet, either open, like a piece of paper, or closed, like the surface of a soap bubble or a red blood cell. While the importance of real biological membranes is well known, physicists are beginning to find that the idealized membranes of which I am going to speak have interesting properties as well.

I shall talk about three classes of systems:

i) Dilute suspensions of closed membranes *without* surface tension, such as red blood cells and quasi-spherical vesicles

ii) The layered phases in oil–water surfactant mixtures

iii) Solutions of two-dimensional polymeric sheets, known as 'tethered surfaces'.

I shall show during my talk that these systems have unusual dynamical properties both near and far from equilibrium. My main results are that all the above systems should have strongly frequency-dependent mechanical properties and that in the layered phases, the application of a sufficiently large velocity gradient should destabilize the phase. I propose various experimental tests of these predictions.

An unconventional mode of repair of DNA damage

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Cellular DNA is subject to many insults, some natural and some deliberate. Some of them are dimerization of adjacent pyrimidines, alkylation of bases, depurination/depyrimidination, interstrand cross-linking, oxidative damage, etc. The enteric bacterium *E. coli* has evolved a number of mechanisms to counter the effects of such damages, even at the risk of suffering mutations. The most thoroughly studied process of DNA repair is the SOS response which repairs damages induced by UV, mitomycin C, some alkylating agents, blocks in DNA replication, etc. The SOS response is under the control of two genes, namely *recA* and *lexA*. Mutations in these genes result in hypersensitivity to DNA-damaging treatments. We have observed that in mutants harbouring a combination of two specific mutations, one in the gene encoding the β subunit of RNA polymerase (*rpoB*) and the other in the gene encoding the A subunit of DNA gyrase (*gyrA*), the hypersensitivity to mitomycin C under SOS-negative and excision repair-defective conditions is largely alleviated. The talk will present data that describe this effect and show that the response is distinctly different from the conventional SOS response. An insertion mutation in a hitherto unidentified genetic locus, which we have named *sir*, results in a reduction in the magnitude of the response but does not abolish it. The mechanism of this repair is not understood at present.

Physicochemical mechanisms controlling engineering properties of clays

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The study deals with the physicochemical mechanisms controlling the engineering behaviour of clays. It is now well established that both attractive and repulsive forces of an electrical nature exist between clay particles and they strongly influence the behaviour of the particles and their aggregations. Repulsive forces between clay particles are primarily attributed to an interaction between double layers. It is of importance to note that this primary force of repulsion increases with an increase in dielectric constant of the medium. The principal contributions to the attractive force come from van der Waals forces and are inversely proportional to the dielectric constant of the medium and the distance between the units.

The conventional 'effective stress' equation should account for the electrical attractive and repulsive forces especially when dealing with cohesive soils. The effective stress equation has been modified to take into consideration the electrical attractive and repulsive forces. Strength and volume change behaviour, the two most important engineering properties, have been shown to be strongly influenced by the electrical forces at particle level with experi-

mental results using fluids of different dielectric constant. The compressiblity/volume change behaviour of clays has been examined in the light of Gouy–Chapman theory of electrical double layer. The effect of hydrated ionic size has been brought out.

It has been shown that the secondary compression coefficient is directly related to the strength of the soil skeleton at particle level which is governed by the modified effective stress. The importance of soil structure/fabric, which is controlled by the electrical forces at particle level, to the physical properties of soils has been brought out.

K-Theory of singular varieties

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A *complex vector bundle* of rank n on a space X is a space E, together with a map $p: E \to X$, whose fibres $E_x = p^{-1}(x)$ are complex vector spaces of dimension n, i.e. $E_x \cong \mathbf{C}^n$.

An affine algebraic variety (over C) is the solution set $X \subset \mathbf{C}^n$ of a system of polynomial equations in n complex variables. An *algebraic vector bundle* on X is a complex vector bundle $p: E \to X$ where $E \subset \mathbf{C}^m$ is also an algebraic variety, and p is a polynomial map. K-theory may be used to study vector bundles on an algebraic variety with singularities.

A basic example is given by a *cone*, which is a variety $X \subset \mathbf{C}^3$ defined by $f(x, y, z) = 0$, where f is homogeneous of degree $d \geq 2$, and the only singular point of X is the origin $(0,0,0)$. It was known that all algebraic vector bundles on X are topologically trivial ($\cong X \times \mathbf{C}^k$ for $k = \text{rank } E$), and this was also true algebraically for cones of degrees 2 and 3. However, using K-theory, it was proved that there exist algebraically non-trivial bundles on cones of degree ≥ 4.

Another problem related to cones is the following. Given a $k \times k$ matrix M with determinant 1 whose entries are polynomial functions on a cone X, can it be reduced to the $k \times k$ identity matrix by row and column operations with coefficients which are polynomial functions on X? K-theory may be used to show that for any cone X (even of degrees 2, 3) there exists an M for which this is impossible.

Sex determination as a developmental problem

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Primary sex determination offers a model system for unravelling the mysteries of development and evolution. It concerns developmental pathways which, in different species, are variously responsive to environmental, genetic or chromosomal factors. In many species of reptiles (alligators, crocodiles and turtles) ambient temperature during the early stages of embryogenesis determines the sex ratio. In amphibia, however, while it is experimentally possible to interfere with the sex-determining process by, for example, hormone administration or grafting of gonadal rudiments, the sex ratio is normally genetically determined. In other groups, genetic control of primary sex ratio has involved the specialization of the entire sex chromosome in respect of this one function (sex determination), and has led to the virtual loss of all its other genetic functions. The investigation of sex chromosomes therefore offers, arguably, the best strategy for approaching one of the most fundamental question in modern biology: how is development controlled? Sex-determining chromosomes, by definition, are chromosomes of known function. The organ system whose development they control are the gonadal rudiments. Within each species, the sexes afford comparisons both at the developmental and at the DNA level, which facilitate identification of the important differences against the background of features common to both sexes. Moreover, mutations that reverse the sex of individuals offer a uniquely valuable system for the study of developmental control.

Recovery of highly conserved sex chromosome-related, repeated DNA (Bkm), originally detected in a female banded krait, and Y chromosome-specific repeat (M34) from male mouse afford accurate means to study development of gonads. Our novel use of sex chromosome-specific probes has revealed that phenotypic sex of an individual mammal, which is determined by the sex of its gonads (i.e. testes or ovaries), is determined by the presence or absence of a small region of the Y chromosome, located near the centromere of the Y chromosome in the mouse. The testis-determining region of the Y appears to exert its primary effect by directing the supporting-cell lineage of the gonad to differentiate as Sertoli cells, acting cell-autonomously.

The phenotypic sex of a germ cell, i.e. whether it undergoes spermatogenesis or oogenesis, is determined by whether or not it enters meiotic prophase before birth. This depends not on its own sex chromosome constitution, but on its cellular environment. A germ cell in or near normal testis cords (made up mainly of Sertoli cells) is inhibited from entering meiosis until after birth; one that escapes this inhibition will develop into an oocyte even if it is in a male animal and itself has XY chromosome constitution.