

Thermodynamics of aqueous solutions (Inaugural address)

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Thermodynamics is a large subject and unquestionably one of the key cornerstones of the chemical engineering science required for the chemical process industry. Due to the importance of the hydrocarbon industry in North America, the thermodynamics of hydrocarbon mixtures, including the non-ideal behaviour, has received attention from early stages. The exciting examples of retrograde condensation and vaporisation may be cited and the peculiar behaviour near critical conditions has been studied. Somehow, as pointed out by a well known American Thermodynamist, the North Americans had not duly recognised "aqueous solutions" notwithstanding its great scientific challenge apart from practical importance. Early work on aqueous solutions included solubility in aqueous electrolyte solutions. The separation of close boiling hydrocarbon mixtures, including olefinic compounds, which at times, even formed azeotropes, provided important scientific challenges resulting in successful exploitation of azeotropic and extractive distillation. Examples included butadiene separation and later benzene separation from other close boiling C_6 hydrocarbons.

Thermodynamics is not an easy subject to teach and a teacher can play an important, if not a pivotal, role in inspiring students to undertake advanced studies in this subject. Indeed the early work done by engineers to develop thermodynamics for heat engines and refrigerants can be cited as impressive examples. Thermodynamics is undoubtedly an intellectually stimulating subject but, as pointed out in a review of the famous book by Guggenheim, it could be "pride and prejudice". It is hoped that deliberations in this Symposium will lead to the well earned "pride".

It is relevant to recall early work on thermodynamics of ammonia synthesis which played a crucial role. So great was its importance, and the suspected non-ideal behaviour, that it led to painstakingly well organised experimental measurements of equilibrium constants leading to pressures approaching 500 atm. It was a welcome relief to find non-idealities leading to increased conversions and this was immensely helpful in industrial practice.

The example of very high pressure polymerisation of ethylene where the solubility data in polymeric melts was required can be cited and here conditions were supercritical. The treatment of sour natural gases to bring down sulphur containing gases like H_2S , COS , CS_2 and mercaptans, in the presence of CO_2 , down to even below 1 ppm can be cited as an outstanding example as multicomponent systems are encountered and the question of primary and secondary equilibrium for carbamate and (even thiocarbamate) formation and subsequent hydrolysis are involved. Computer simulations became a necessity. Equally interesting was the example of azeotropic distillation of benzene from its mixtures with close-boiling C_6 hydrocarbons where whether benzene will come as an overhead product or a bottom product had to be settled. Most recently we have distillation column reactors, with packings made of catalytic materials like ion-exchange resins, to carry out combined reactions and distillations (e.g. MTBE) in equilibrium limited highly non-ideal systems.

In the recent past a lot of excitement has been generated due to the commercial importance of supercritical extraction of a variety of expensive substances. Here a novel idea has been the role of entrainers. The supercritical extraction has been relevant in hydrocarbon processing for a long time as the example of propane deasphalting will indicate. Supercritical fluid chromatography is another novel use in analysis and separation of biological systems.

A lot of interest has been generated by the rather accidental discovery of partitioning proteins in aqueous-aqueous systems involving polyethylene glycols, dextrans, magnesium salts etc. From a chemical engineering standpoint these systems have provided a lot of challenges as in solvent extraction columns the interfacial tension will be at vanishing level and the density difference is also small. The downstream processing in biotechnology offers many opportunities. Even the separation of proteins through focussing isoelectric points can be cited as an example.

The world of interface science has provided its own excitement through the thermodynamics of micelles formation and lately we have the fascinating world of microemulsions. Our predictive capabilities are on a trial. The role of hydrotropes in enhancing solubilities requires a closer look.

The subject of wastewater treatment and the fate of chemicals after release in air, water or land itself provides a bunch of complicated systems. The predictions of partition coefficients in *n*-octanol-water system, which also happens to be relevant in some ways in the delivery of drugs, by the group-contribution method can be considered as an important step in our predicting capabilities. We have seen success in predicting ionisation constants of a variety of acids and bases and heat and free energy of formations of a myriad range of compounds. The prediction of adsorption equilibrium in multicomponent systems offer challenges and these are commercially important. We are now required to predict thermodynamic data for a variety of solutes in aqueous solutions for steam stripping leading to really vanishing levels of the solute and here often multiple solutes are involved.

The developments in computation methods have been a boon for scientist working on thermodynamics. The ease with which UNIQUAC, ASOG, UNIFAC, etc. methods can be deployed needs to be appreciated.

The emerging field of membranes based separations, including pervaporation, has kindled the interest in solubility in polymeric systems and shining examples of H₂—CO₂ and O₂—N₂ separations and breaking of alcohol-water azeotrope by pervaporation may be cited.

It is very encouraging to find scientists from all over the world participating in this IUPAC Symposium and it is hoped that the participants will find a rich menu.