Role of Chemical Reaction Engineering in Sustainable Process Development*
(Addendum CHE 505)
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1. Introduction

Achieving sustainable processes, that allow us at present to fully meet our needs without impairing the ability of future generations to do so, is an important goal for current and future engineers. In production of new materials, chemicals, and pharmaceuticals sustainable processes certainly require the most efficient use of raw materials and energy, preferably from renewable sources, and prevention of generation and release of toxic materials. Advancing the state of the art of chemical reaction engineering (CRE) is the key element needed for development of such environmentally friendly and sustainable chemical processes.

Current chemical processes depend heavily on the non-renewable fossil-based raw materials. These processes are unsustainable in the long run. In order to make them sustainable, chemical technologies must focus on employing renewable raw materials as well as preventing and minimizing pollution at the source rather than dealing with end-of-pipe treatments. New technologies of higher material and energy efficiency offer the best hope for minimization and prevention of pollution. To implement new technologies, a multidisciplinary taskforce is needed. This effort involves chemical engineers together with environmental engineers and chemists since they are predominantly in charge of designing novel chemical technologies.

Pollution prevention problem can be attacked via a hierarchical approach based on three levels as outlined in the book by Allen and Rosselot. Each level uses a system boundary for the analysis. The top level, (the macro-level) is the largest system boundary covering the whole manufacturing activity from raw material extraction to product use and eventually disposal. These activities involve chemical and physical transformation of

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raw materials creating pollution or wastes as shown schematically in Figure 1. The scope of the macro-level analysis is mainly in tracking these transformations, identifying the causes of pollution and suggesting the reduction strategies.

The next level is the plant level or the meso-scale which is the main domain of chemical engineers. The meso-level focuses on an entire chemical plant, and deals with the associated chemical and physical transformations of non-renewable resources (e.g. petroleum and coal, etc.) and renewable resources (e.g. plants and animals) into a variety of specific products. These transformations can result in a number of undesirable products which, if not checked, can result in pollution of the environment. The challenge then for modern chemical engineers is to improve the efficiency of existing processes, to the extent possible, and design new cleaner and more efficient processes. While in the past the effort was focused on end of the pipe clean-up and remediation, the focus now is on pollution prevention and ultimately on sustainability. Mass and energy transfer calculations as well as optimization of processes that result in less pollution can be performed at this level. This plant scale boundary usually consists of raw material pretreatment section, reactor section, and separation unit operations. (See Figure 2.) Although each of these sections are important, the chemical reactor forms the heart of the process and offers considerable scope for pollution prevention. The present paper addresses the scope for pollution prevention in the reactor unit and sustainable development. It may however be noted that the reactor and separator sections are closely linked and in some cases, improvements in the reactor section may adversely affect the separation section leading to an overall increase in pollution. Hence any suggested improvement in the reactor section has to be reevaluated in the overall plant scale context.

The third level indicated by Allen and Rosselot\textsuperscript{1} is the micro-level that deals with molecular phenomena and how it affects pollution. Analysis at this scale includes synthesis of benign chemicals, design of alternative pathways to design a chemical, etc. CRE plays a dominant role at this level as well and some applications of CRE at the micro-level pollution prevention are also indicated in the paper.

Waste reduction in chemical reactors can be achieved in the following hierarchical manner: (i) better maintenance, (ii) minor modifications of reactor
operation, (iii) major modifications or new reactor concepts and (iv) improved process chemistry, novel catalysts and use of these in suitable reactors. The items (i) and (ii) are usually practiced for existing plants while items (iii) and (iv) above are more suitable in the context of new technologies or processes. Also items (iii) and (iv) involve a multidisciplinary R&D activities which can be costly. But since long-term sustainability is the goal this is a worthwhile effort and increasing activities are expected in this direction in the future. The items (i) and (ii) are addressed in a paper by Dyer and Mulholland² and this paper focuses mainly on (iii) and (iv).

It is also appropriate at this point to stress the multi-scale nature of reaction engineering. Figure 3 shows the multi-level CRE approach. We have at the tiniest scale the catalytic surface up to macro-scale of huge 10m high chemical reactor and hence the task of pollution prevention in chemical reactor is a formidable task and has to address phenomena at all these scales. At the molecular level, the choice of the process chemistry dramatically impacts the atom efficiency and the degree of potential environmental damage due to the chemicals produced. We will first review how some micro-level concepts such as atom efficiency (Section 2) and optimum catalyst development (Section 3) affect reactor choice and pollutants generated. At the meso-level, optimizing the catalyst properties (Section 3) and choosing the right media (Section 4) significantly reduces the adverse environmental impact of chemical processes. Clearly, proper understanding and application of the principles of multiphase reaction engineering are very important for proper execution of truly environmentally benign processes since almost all processes involve more than one phase. At the macro-level, it is crucial to estimate the hydrodynamic effects (Section 5) on reactor performance as this will lead to the selection of the right reactor. Furthermore, novel approaches to reactor design using process intensification concepts (Section 6) can be implemented to improve efficiency and minimize pollution. In addition, environmental impact analysis (Section 7) of the developed process has to be evaluated to see if green chemistry conditions are met and to assess the overall global impact of these changes. As can be seen, CRE is a marriage of multidisciplinary and multi-scale efforts with the aim of operating at sustainable green chemistry conditions to reduce pollution and maximize efficiency. The summary of these efforts and conclusions are given in Section 8.
2. Raw Materials Selection

The aim of benign synthesis is to reduce the amount of side reactions generating undesired by-products, i.e. waste. Alternative direct synthetic routes are therefore advantageous from the point of waste reduction and have an economic advantage. The organic chemistry is rich with reactions where large quantities of inorganic salts are generated as wastes that lead to poor atom efficiency. These can be avoided by selecting raw materials appropriately. Therefore, using environmentally benign raw materials can make a big impact on pollution prevention and thus enhance sustainability. Atom and mass economy calculations, that measure how efficiently raw materials are used, are the key decision-making concepts in selection of raw materials for a given process.

To give an example, two raw materials, benzene and n-butane can be employed in the production of maleic anhydride (the first step to produce maleic acid). The following reactions are possible routes to maleic anhydride.

**Benzene route:**

\[ 2C_6H_6 + 9O_2 \xrightarrow{V, O_{2}, MoO_3} 2C_4H_2O_3 + H_2O + 4CO_2 \]

**n-butane route:**

\[ C_4H_{10} + 3.5O_2 \xrightarrow{(VO)_2P_2O_7} C_4H_2O_3 + 4H_2O \]

In the benzene route, there are four carbon atoms in product maleic anhydride per 6 carbon atoms in benzene. Therefore, the atom efficiency for the carbon atom is \( \frac{4}{6} \times 100\% = 66.7\% \). In the n-butane route, there are four carbon atoms in n-butane per four carbon atoms in maleic anhydride thus giving 100% atom efficiency.

If mass efficiency is considered, then the mass of the product is compared to the mass of the raw materials. The molecular weight of maleic anhydride is 98. For the n-butane route, we need 1 mole of n-butane (molecular weight 58) and 3.5 moles of oxygen (total mass of 3.5 x 32 = 112.) Thus the total mass of raw materials needed is 170. The mass efficiency of the n-butane route is therefore 98/170 or 57.6%. By a similar calculation, we can show that the mass efficiency of the benzene route is only 44.4%.
As can be seen, n-butane is favorable to benzene in comparison of both atom and mass economy. In addition, benzene is expensive and toxic. Therefore n-butane has replaced benzene in maleic anhydride production since the 1980s. A detailed case study comparing the two routes is given in the Green Engineering book³.

Choosing benign and efficient raw materials is the first step in designing environmentally friendly processes. Once the process route is selected, the process yield and efficiency can be further improved and pollution can be minimized more effectively by the proper choice of catalyst and solvents used. Issues related to catalyst selection and development are discussed next.

3. **Catalyst Selection, Development and Reactor Choice**

   Catalysts are being used extensively in chemical and fuel industries. Hence, selecting and developing the right catalyst has a huge impact on the success of a proposed process route. However, it may be noted that the development of novel catalyst has to be often combined with novel reactor technology for the process to be economically viable and environmentally beneficial. Hence catalyst development and reactor choice often have to be considered in unison.

   As a general heuristic rule, the processes that replace liquid routes by solid catalyzed routes reduce pollution significantly especially when the some of the liquid reactants are toxic. For example, many liquid acids such as H₂SO₄ and HF used as catalysts in petroleum refining industry impose a significant environmental hazard as they are highly corrosive and toxic. Therefore, based on environmental concerns these catalysts are now being replaced by solid-acid catalysts.

   Once selected, to further tailor the catalyst to get optimum yield and selectivity, physical properties of the catalyst have to be determined and improved. Experimental methods, namely NMR, spectroscopy, kinetic measurements are available to study important properties such as the surface topology of the catalyst, the adsorption sites and how the molecules are adsorbed on the catalyst surface. Computer simulations of pore structure are also becoming increasingly popular to study the transport behavior of the catalysts. Detailed micro-kinetic modeling using molecular dynamic simulations are also useful to guide the design of a new catalyst.
Examples of catalyst development and appropriate reactor selection are illustrated in the following discussions by consideration of oxidation and alkylation which are two common reaction types in organic synthesis.

**Oxidation:**

Oxidation reactions are important in producing many fine chemicals, monomers and intermediates. \( \text{O}_2, \text{H}_2\text{O}_2 \text{ and HNO}_3 \) are common oxidants used in these reactions, with oxygen being the most benign oxidant. We will particularly talk about \( \text{n-butane} \) oxidation to maleic anhydride in this section and discuss the reactor choice for vanadium phosphorous oxide (VPO) catalyst.

Initially, fixed bed reactor configurations were used for this process. Fixed bed catalytic reactor is one of the most utilized reactors in the petrochemical and petroleum refining industry. These reactors use solid catalysts in pellet or granular form and they can be visualized as shell and tube heat exchangers. There are several limitations in employment of fixed bed catalytic reactors. The reactors are expensive and only up to 2 \% \( \text{n-butane} \) can be used in the feed\(^4\). Yield is around 50 \% with 70-85 \% conversion and 67-75 \% molar selectivity to maleic anhydride\(^4\). Moreover, since the reaction is exothermic, hotspot formation must be avoided. Reactor designs have advanced to a point where some of these issues can be addressed effectively. Catalyst development has also progressed and the yield and selectivity have improved over the years by controlling the chemical composition and morphology of the catalyst. However, it may be noted that, the mechanical properties of the catalyst is equally important. The catalysts used in packed beds are usually supported metals from 1 to 10 mm in size. These must have adequate crushing strength to carry the full weight of a packed bed.

In order to minimize hotspots, fluidized catalyst beds are preferred over fixed catalyst beds. The advantages of fluidized catalyst beds include the ease of temperature control, superior heat transfer and lower operating temperatures compared to fixed catalyst beds. In a fluidized catalyst bed, higher butane concentrations (up to 4\%) are handled reducing operating costs\(^4\). The disadvantage of the fluidized catalyst bed is the rapid reduction of the catalyst surface, catalyst attrition and carry over of fines leading to air pollution. Again the mechanical properties of the catalyst play an important role. In
fluidized beds, much smaller (compared to packed bed) catalyst particles on support (20 to 150 μm) are used and these must exhibit outstanding attrition properties. Hence, extensive catalyst development was required to move butane oxidation from fixed to fluidized beds.

In the mid 1990s, another improvement by DuPont de Nemours\textsuperscript{5} in reactor design introduced circulating fluid bed (CFB) technology to maleic anhydride production. The incentive for this change was provided by the realization that much higher productivity and selectivity can be obtained by using the catalyst in transient rather than steady state operation. CFB provides an ideal reactor set-up for such cyclic transient operation. In this reactor configuration, the chemistry is executed in a fluid bed-riser combination to accommodate successive oxidation and reduction of the catalyst. In the riser, n-butane gets converted to maleic anhydride while the catalyst gets reduced from V\textsuperscript{+5} to V\textsuperscript{+3} given by the scheme as:

\[
\begin{align*}
V^{+5} & \xrightarrow{\text{HC}} V^{+4} \xrightarrow{\text{HC}} V^{+3}
\end{align*}
\]

The reduced catalyst then circulates to the regenerator where it contacts air and gets oxidized back to V\textsuperscript{+5} given by the scheme as:

\[
\begin{align*}
V^{+3} & \xrightarrow{O_2} V^{+4} \xrightarrow{O_2} V^{+5}
\end{align*}
\]

In this way, n-butane and oxygen are not in direct contact and this leads to minimizing side reactions and higher maleic anhydride selectivity (up to 90 \%) is therefore obtained\textsuperscript{4,6}. Figure 4 shows the circulating fluid bed reactor configuration. Again, to enable the use of CFB extensive catalyst development took place to introduce a highly porous but extremely attrition resistant shell on the VPO type catalyst.

VPO catalyst has also been subject to detailed investigation to further optimize its physical properties. For example, Mota \textit{et al.}\textsuperscript{7} investigated modifying VPO catalyst by doping with Co or Mo to operate under fuel-rich conditions (i.e. O\textsubscript{2}/C\textsubscript{4}H\textsubscript{10} = 0.6). The authors state that Co-doped VPO catalyst performed better than the Mo-doped VPO catalyst and did not deactivate as the original VPO catalyst.

\textbf{Alkylation:}

Hydrocarbon alkylation reactions are important in petroleum industries for producing high octane gasoline stocks. Traditional routes use liquid phase acids such as
HF or H₂SO₄ or Lewis acid metal halides such as AlCl₃ and BF₃. In these reactions, stoichiometric quantities of acids and/or halides are often needed and generate massive corrosive and toxic effluents. Alkylation reactions are, therefore, excellent targets for new cleaner chemistry.

There has been a significant development in the reactor design in liquid phase processes to lessen the environmental risks. In the original process, stirred tanks (mixer settlers with heat exchanger), operated in parallel to keep olefin concentration low, were used with HF being the catalyst. Figure 5 shows the schematics where HF is recycled with an external pump. Due to HF use and leaky seals on the pump and reactor mixing shafts, this process is environmentally unfriendly. The newer reactor solved this problem by utilizing an HF internal recycle. This design accomplished mixing by utilizing the buoyancy force created in the mixture of a heavy (HF) and light phase (hydrocarbon paraffin-olefin mixture). Unfortunately, the process is still environmentally unfriendly due to presence of HF. The challenge is to develop a stable solid catalyst that will be effective and regenerable as the conventional HF/H₂SO₄ catalyst that is still employed worldwide.

Common types of solid acids are the Beta zeolites, ion exchange resins, such as silica, supported nafion and heteropoly acids such as tungsto-phosphoric acids. However, these catalysts are easily deactivated and must be reactivated each time. Hence, complex reactor types must be designed so that the reaction and regeneration activities can be combined. Circulating fluid beds, packed beds with periodic operation, stirred tanks with or without catalyst baskets and chromatographic reactors are types of reactors that have been considered. Figure 6 shows a circulating fluid bed which is similar in concept to the reactor used in maleic anhydride production.

In order to select the best reactor among these reactor types, reactor models based on hydrodynamics, kinetics and pore diffusion must be accounted for since transport resistances may play a significant role in reactor performance. Therefore, proper understanding of these factors is a must to interpret the product selectivity and extent of formation of waste products. An additional discussion of transport resistance is in Section 5.
4. Solvent selection

As a general guideline, for an improved process reactor design, the use of solvents should be reduced and benign solvents should be employed if necessary. With these guidelines in mind, much attention has been given to “green” solvents such as supercritical CO$_2$ (scCO$_2$) and ionic liquids with the hope that they will replace the current solvents that cause pollution.

scCO$_2$ is environmentally friendly as it is non-toxic, unregulated, and non-flammable. It is also preferable as it is ubiquitous and inexpensive. scCO$_2$ has been extensively used in oxidation reactions. However, scCO$_2$ based oxidations are limited by low reaction rates. Further the homogeneous catalysts needed in the reaction have limited solubility in scCO$_2$. Hence, the use of expanded advents is being advocated for homogeneous catalytic oxidations and currently there has been a shift in the research to use the CO$_2$-expanded solvents for many organic processes. Advantage of CO$_2$-expanded solvents is that the process pressure can be significantly lower compared to scCO$_2$. By changing the amount of CO$_2$ added, it is possible to generate a continuum of media ranging from the neat organic solvent to pure CO$_2$. Wei et al. have studied the solubility of O$_2$ in CO$_2$-expanded CH$_3$CN and found that it was two times higher compared to neat CH$_3$CN, resulting in maximizing oxidation rates. The authors also reported that conventional organic solvent was replaced up to 80%. Hence CO$_2$-expanded solvents look promising in replacing the current solvents that are not environmentally friendly. More research is still needed in this area to enable scale-up and commercialization.

Ionic liquids are solvents that have no measurable vapor pressure. They exhibit Brønsted and Lewis acidity, as well as superacidity and they offer high solubility for a wide range of inorganic and organic materials. The most common ones are imidazolium and pyridinium derivatives but also phosphonium or tetralkylammonium compounds can be used for this purpose. Classical transition-metal catalysed hydrogenation, hydroformylation, isomerisation, dimerisation can be all performed in ionic liquid solvents. The advantages of ionic liquid solvents over conventional solvents are the ease of tuning selectivities and reaction rates as well as minimal waste to the environment. As with scCO$_2$, more research is needed in scale-up and
commercialization as well as in investigating different types of ionic liquid solvents for other catalytic reactions.

5. **Reactor Design**

Choice of reactor type should be made in the early stages of process and catalyst development. It should consider the kinetic rates achievable and their dependence on temperature and pressure, the transport effects on rates and selectivity, the flow pattern effect on yield and selectivity as well as the magnitude of the needed heat transfer rates. Then plug flow or perfect mixing is identified as ideal flow pattern that best meets the process requirements in terms of productivity and selectivity. The final reactor type is chosen so as to best approach the desired ideal flow pattern and provide the needed heat transfer rates. The reactor should not be overdesigned to reach the desired product selectivity and to minimize waste generation. Therefore, sophisticated reactor models have been developed as essential tools for reactor design and scale-up. For these models to be accurate, information on volume fraction (holdup) distribution, velocity and mixing of the present phases has to be known. This hydrodynamic information is then coupled with kinetics of the reaction and deactivation to develop a sophisticated reactor model.

There are several experimental measurement techniques to get information on velocity and turbulence parameters in gas-solid, gas-liquid, liquid-solid, and gas-liquid-solid systems. Computed Tomography (CT) and Computer Automated Radioactive Particle Tracking (CARPT) are non-invasive measurement methods well suited for providing information needed for validation of CFD codes and reactor model development. Figure 7 gives the schematics of these experimental techniques. CT experiments are used to obtain density distribution and CARPT experiments to obtain the velocity field and mixing information\textsuperscript{12,13}.

Hydrodynamic information obtained from CT and CARPT experiments can then be applied to reactor models. For example, for a liquid-solid riser, there are four reactor models at different sophistication levels: heterogeneous plug flow model (as the simplest), 1-D axial dispersion model, core annulus model and 2-D convection-dispersion model as the most complex. Each model requires an appropriate set of hydrodynamic parameters. The CT and CARPT provide these and combining this data...
with the kinetics of reactions and deactivation of the catalyst, one can develop detailed models to guide the selection and design of catalytic riser reactors.

6. Process Intensification

Process intensification involves design of novel reactors of increased volumetric productivity and selectivity. The aim is to integrate different unit operations to reactor design, meanwhile operating at the same or better production rates with minimum pollution generation. To meet these goals, the practice involves utilization of lesser amount of hazardous raw materials, employing efficient mixing techniques, using microreactors, catalytic distillation, coupling of exothermic and endothermic reactions and periodic operations. As examples consider catalytic distillation and coupling of exothermic and endothermic reactions.

*Catalytic distillation:*

Catalytic distillation has been employed successfully for ethylacetate, H$_2$O$_2$, MTBE, and cumene production. The catalytic distillation unit consists of rectifying and stripping sections as well as a reaction zone that contains the catalyst. The column integrates separation and catalytic reaction unit operations into a single unit therefore reducing capital costs. It is also beneficial in the fact that separation reagents that are toxic are no longer required. Since unreacted raw materials are recycled, less amount of feed is converted to products, thus reducing the use of harmful raw materials and waste generation. Significant energy savings due to utilizing the heat released by exothermic reaction for distillation is also another factor that contributes to this unit being environmentally friendly.

An application to ketimine production scheme using a catalytic distillation unit is illustrated in Figure 8. Condensation of ketones with primary amines results in the synthesis of ketimines given by the reaction scheme:

$$R-NH_2 + R-N \xrightarrow{O} R-N + H_2O$$
The reaction is reversible and therefore equilibrium limited. In the conventional process, the reversible reaction can be pushed forward to products by employing drying agents such as TiCl$_4$, BuSnCl$_2$, Al$_2$O$_3$ and molecular sieves which remove the product water. By using catalytic distillation, ketones and amine react to produce ketimine. Excess ketones are recycled back and product water is separated via in situ separation. No drying agents are needed thereby making the process cost efficient and environmentally friendly.

**Coupling of exothermic and endothermic reactions:**

Using heat integration is another important guideline for improved reactor design and is another example of process intensification. Exothermic and endothermic reactions can be combined together in a reactor configuration to maximize energy conversation in the process. As an example, steam reforming of methane, an endothermic reaction (Reaction 1) can be combined with partial oxidation of methane, an exothermic reaction (Reaction 2).

\[
CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \text{(Reaction 1)}
\]

\[
CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \text{(Reaction 2)}
\]

The coupled reactions can be carried out in a shell and tube exchanger design that improves the energy efficiency of the process. This leads to a compact design. By contrast conventional steam reforming require huge furnaces leading to large capital cost and loss of energy.

Additional examples of process intensification such as microreactors, disk and plate reactors and reactive membranes can be found at Tsouris *et. al.* and Reaction Engineering for Pollution Prevention book.
7. Environmental Impact Analysis

Once new chemical processes are developed, catalyst, solvent and reactor type selected using CRE methodology, the impact on the environment of the new chemical processes must be compared with the impact of conventional processes before implementation of the new process. Several tools such as Waste Reduction Algorithm (WAR)\textsuperscript{20,21}, Life Cycle Analysis (LCA)\textsuperscript{22} and Environmental Fate and Risk Assessment Tool (EFRAT)\textsuperscript{23} are available for environmental impact analysis. Much research is devoted to improve the accuracy of these tools and to develop a standard methodology.

The WAR algorithm is used for determining the potential environmental impact of a chemical process based on 9 different impact categories listed in Table 1.

Table 1. Potential environmental impact categories

<table>
<thead>
<tr>
<th>Physical Potential Effects</th>
<th>Acidification</th>
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<tbody>
<tr>
<td></td>
<td>Greenhouse Enhancement</td>
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<tr>
<td></td>
<td>Ozone Depletion</td>
</tr>
<tr>
<td></td>
<td>Photochemical Oxidant Formation</td>
</tr>
<tr>
<td>Human Toxicity Effects</td>
<td>Air</td>
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<tr>
<td></td>
<td>Water</td>
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<td></td>
<td>Soil</td>
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<tr>
<td>Ecotoxicity Effects</td>
<td>Aquatic</td>
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<tr>
<td></td>
<td>Terrestrial</td>
</tr>
</tbody>
</table>

Potential environmental impact is a conceptual quantity that arises from energy and material that the process takes from or emits to the environment\textsuperscript{24}. The impact categories listed in Table 1 are weighted according to local needs and policies, and the scores are normalized to eliminate bias within the database. The WAR is particularly useful for comparison of different existing processes but does not provide modifications that would minimize the waste. Application examples of WAR studies include methyl ethyl ketone production from secondary butyl alcohol\textsuperscript{24,25}, ammonia production from synthesis gas\textsuperscript{25}, and reactive distillation for butyl acetate production\textsuperscript{26}. 
The LCA has been developed to understand and characterize the range and scope of environmental impacts at all stages within a product or process. LCA basically evaluates the process based on the boundaries of the assessment. Life cycle inventories for the inputs, products and wastes are evaluated for the system boundary. The results then can be compared for different chemical processes. LCA is very useful for global analysis shown in Figure 1.

EFRAT is a simulation package developed by the EPA. It is used to estimate the environmental and health impacts of chemical process design options through a combination of screening-level fate and transport calculations and risk assessment indices. EFRAT is a powerful simulation tool as it provides the process design engineer with the required environmental impact information, so that environmental and economic factors may be considered simultaneously.

CRE together with green engineering principles provide the key concepts in designing and operating chemical processes at sustainable conditions. The improved process, however, must also be examined under close scrutiny by using the tools mentioned above. The results must be compared to conventional processes to see if the overall environmental impact has been reduced.

8. Summary and Conclusions

In our road to achieving sustainability in production of materials and chemicals we must strive to eliminate pollution at the source, improve material and energy efficiency of our processes and use renewable resources. The best way to prevent pollution is at the source. Thus, if we want to have high tech processes that are “sustainable” and “green”, we must use chemical reaction engineering concepts to the fullest extent. The days when the chemist found a magic ingredient (catalyst) for a recipe and the chemical engineer tried in earnest to get its full potential expressed in an available ‘kettle’, must be replaced by the coordinated effort of the chemist to select the best catalyst and the chemical engineer to provide the best flow pattern and reactor. This effort requires the multi-scale CRE approach consisting of molecular, particle/eddy and reactor scale considerations.
Since the last decade, the chemical reaction engineers have been re-focusing on developing new technologies that prevent or minimize pollution rather than dealing with ‘end of pipe’ treatments. In order to develop such technologies, a quantitative understanding of reaction systems and transport properties on the reaction rates is a must. Furthermore, the physical properties of the catalyst and media are also determining factors in choosing the “right” reactor for an environmentally benign process. Hence, it is a multidisciplinary task combining chemistry, reaction engineering, environmental impacts and economics. This chapter outlined the multi-scale nature of the CRE approach starting from the molecular level at the atom efficiency to the process level at the scale-up of a reactor. Each scale is important in design and operation of a sustainable process. The combination of CRE approach with “green processing” principles should lead to the development of a sustainable chemical industry with minimal waste production.

**Acknowledgements**

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Figure 1. Schematic of chemical and physical transformations causing pollution or wastes.
Figure 2. Schematic of system boundaries. The first figure shows the global scale and the second one shows the plant scale. The reactor itself constitutes another boundary that chemical reaction engineers focus on.
Figure 3. Schematic of integrated multi-level CRE approach. All the above levels are important in design and operation of a successful reactor.
Figure 4. Circulating Fluid Bed reactor used for maleic anhydride production.

Figure 5. Reactor types for liquid phase alkylation process
Figure 6. Novel reactor type for solid acids.
Figure 7. Computer Automated Radioactive Particle Tracking (CARPT) and Computer Tomography (CT) experiments
Figure 8. Ketimine production by catalytic distillation.

MIBK: Ketones
EDA: Amine
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1.1 Introduction

Chemical reactions play a key role in generation of pollutants (e.g. combustion of fossil fuels) as well as in pollution abatement (e.g. automobile exhaust catalytic converter). Hence, the understanding of reaction systems, is necessary in environmentally conscious manufacturing, in "end of the pipe treatment" of pollutants, “in-situ” pollution remediation and in modeling global effects of pollutants. Quantitative understanding of chemical reactions involves two cornerstones of physical chemistry: chemical thermodynamics and chemical kinetics. The principles of thermodynamics define composition at equilibrium, i.e. the condition towards which every closed system will tend. Chemical kinetics quantifies the rate at which equilibrium is approached. Both thermodynamic and kinetic concepts are needed for a full quantification of pollution generation and abatement phenomena, where rate processes are often dominant over thermodynamic considerations. Prediction of air quality and water quality, as well as the quantification of the effects induced by humans, and of the natural processes, on the whole ecosystem, also require good understanding of reaction systems. In addition to being able to predict how far a reaction can proceed and at what rate, it is also important, when dealing with pollution prevention and remediation, to be able to assess the effect of physical transport processes (e.g. diffusion, heat transfer, etc.) on the reaction rate and "engineer a reaction system" in a desirable way. The study of reaction rates and engineering of reaction systems pertinent to environmental control or remediation, is the subject of this book. Since this text is meant for students in science and engineering of diverse backgrounds who are interested in the environment, we will start with the most fundamental concepts first and attempt to explain them in the simplest terms. Then we extend these concepts and illustrate their use in engineering practice. MATLAB based simulation tools are also provided to facilitate learning the concepts.

Understanding chemical, photochemical, biochemical, biological, electrochemical and other reactions and their rates and the rates of associated physical transport processes, is important in reaction systems involved in:

- pollution generation in chemical processes;
- pollution abatement via end of the pipe treatment;
- waste water treatment;
- fate of pollutants in the environment;
- pollutant dynamics in the atmosphere;
- pollutant dynamics in aquatic systems;
- global and regional pollutant dynamics.
The scope of this chapter is to introduce the pertinent chemistry involved in some of these processes and provide a perspective on the knowledge base needed to do some of these studies.

1.2 Reactions leading to generation of pollutants

There are several sources of pollution: Carbon monoxide and nitrogen oxides emitted as exhaust from cars, SO$_2$ released in power plant flue gases, emissions from the chemical industry, etc. Figure 2 gives a simplified schematic for the pollution cycle.

![Figure 2: The cycle of pollution](image-url)
1.3 Impact of Pollutant and Their Reactions on the Environment

In this section, we introduce examples of the impact of pollutants in the environment. In particular, we focus on ozone depletion, smog formation and acid rain. Let’s start with ozone depletion.

1.3.1 Ozone Depletion

In general, the concentration of gases such as CH$_4$, CO, CO$_2$, NO$_x$, and SO$_2$ has increased over this century and the reason for this is a cumulative effect of combustion, automobile exhaust and other human activities such as farming, deforestation, increased biomass activity due to landfills, etc. The chemical industry also contributes to the atmospheric pollution, but is not the sole culprit.

Gases, which are relatively insoluble and unreactive readily spread through the troposphere (lower 10-15 km of earth) and in some cases, find their way to the stratosphere (10-50 km above the surface). Figure 3 gives a schematic of atmospheric reactions in the troposphere and stratosphere.

Figure 2. Spreading and reactions of pollutants in troposphere and stratosphere.
It is important to note that ozone can be “good” or “bad” depending on where it is in the atmosphere. The “good” ozone shields the earth’s surface from intense ultraviolet radiation and is located in the stratosphere. The chlorine atoms released from CFC (chlorofluorocarbons) play a critical role in the destruction of the protective ozone layer.

In the stratosphere UV radiation is intercepted by ozone which then decomposes naturally into oxygen by a simple mechanism.

\[
\begin{align*}
O_3 & \xrightarrow{hv} O^* + O_2 \\
O^* + O_3 & \rightarrow 2O_2
\end{align*}
\]

The rate of this natural decomposition of ozone is much enhanced by the presence of chlorofluorocarbons (CFC) as follows:

\[
\begin{align*}
CFC & \xrightarrow{hv} ClO + Cl^* \\
O^* + ClO & \rightarrow Cl^* + O_2 \\
O_3 + Cl^* & \rightarrow O_2 + ClO
\end{align*}
\]

This catalytic cycle by which ClO is continuously regenerated enhances ozone decomposition almost 200 times at temperatures of around 200K in the stratosphere. In this course we will be learning how to deal with mechanisms in deriving the rates of reaction and how to estimate these rates.

The ozone depletion is a great concern since ultraviolet radiation can be very harmful to crops, trees, animals and people.

The “bad” ozone is located in the troposphere and is produced photolytically with help from nitrogen oxides as can be seen from the following reaction scheme.

Photolytic production of ozone:

\[
\begin{align*}
NO_2 + UV & \rightarrow NO_2^* \\
\text{(small amount)}
\end{align*}
\]

\[
\begin{align*}
NO_2^* & \rightarrow NO + O^* \\
O^* + O_2 & \rightarrow O_3
\end{align*}
\]
The ozone produced then reacts with nitrogen oxides and hydrocarbons resulting in smog creating aldehydes and other oxidation products.

Reactions of ozone:

\[ O_3 + NO \rightarrow NO_2 + O_2 \]

\[ O_3 + HC \rightarrow \text{Aldehydes and other oxidation products} \]

### 1.1.1 Smog Formation

Photodissociation of NO\(_2\) is responsible for lower atmosphere ozone formation. NO formed combines back with O\(_3\) keeping a steady state level for O\(_3\).

\[ O_3 + NO \rightarrow NO_2 + O_2 \]

Thus, our acceptable level of O\(_3\) is maintained in the absence of atmospheric pollutants such as VOC or excessive nitrogen oxide concentration (we will see later that ozone “tracks” \( NO_2/NO \) ratio).

The role of Volatile Organic Compounds (VOCs) is to form radicals that convert NO to NO\(_2\), without the need for ozone, as can be seen in the following reaction scheme.

\[ VOC + \cdot OH \rightarrow \cdot RO_2 + \text{other oxidation products} \]

\[ RO_2 \cdot + NO \rightarrow NO_2 + \text{radicals} \]

As the concentration of VOC increases, NO\(_2\)/NO ratio and ground level “bad” ozone levels also increase. The increased ozone formation leads to the following reaction

\[ O_3 + HC \rightarrow \text{Aldehydes and other oxidation products} \]

leading to smog formation.

The rate constant for the formation of hydroxyl radical is a measure of smog formation potential. Estimation methods for the rate constants will be reviewed later. Incremental reactivity scale is a measure of contribution of various groups to the rate of VOC reaction with OH\(^\circ\) radicals and is often
used a measure of smog formation potential of any particular chemical. The formal definition of incremental reactivity is the change in moles of ozone formed as a result of emission into air-shed of one mole (on a carbon atom basis) of the VOC. Such considerations are important in assessing the environmental impact of any chemical being used in, for example, consumer products. It may also be noted that 0H° radicals are normally present in the atmosphere to facilitate the reaction with VOCs. The concentration is very small but significant enough to cause smog.

1.1.2 Acid Rain

Rain water is supposed to be pure of distilled water-like quality but gets contaminated by interaction with pollutants in the air. Best known examples of such contaminations are acids generated from NOx and SOx emissions. The distribution of these and other pollutants (once they are released into the atmosphere) depends on gas-liquid equilibrium: partition or solubility coefficient. Thus, the pollutants seek out and concentrate in the medium in which they are most soluble. The insoluble gases may react with other components present in the air environment. Soluble gases such as SO2, released as part of flue gases, are absorbed in water droplets (rain, snow, fog or dew) rain. Dissolved SO2 in water droplets reacts to form SO3 and subsequently H2SO4. These SO2 conversion reactions are schematically represented in Table 1 and result in acid rain.

<table>
<thead>
<tr>
<th>Reactions of SO2 in the environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>( SO_{2(g)} \rightarrow SO_{2(aq)} )</td>
</tr>
<tr>
<td>( SO_{2(aq)} + H_2O \leftrightarrow H^+ + SO_3^- )</td>
</tr>
<tr>
<td>( HSO_3^- \leftrightarrow H^+ + SO_3^- )</td>
</tr>
<tr>
<td>( O_{2(g)} \leftrightarrow O_{2(aq)} )</td>
</tr>
<tr>
<td>( SO_3^- + \frac{1}{2} O_{2(aq)} \rightarrow SO_4^- )</td>
</tr>
</tbody>
</table>

Acid rain is thus formed predominantly by the oxides of sulfur and nitrogen. The later also catalyze sulfuric acid formation. The basic sources of sulfur dioxide and nitrogen oxides are indicated below:
Sulfur dioxide (SO$_2$) in the atmosphere results from:
- oxidation in the course of combustion of fossil fuels
- former “Kraft” process for paper manufacture
- natural emissions of biological origin such as dimethyl sulphide and hydrogen sulphide
- physical coal cleaning (PCC) plants
- fluid catalytic cracking: (FCC) off gases

Nitrogen oxides (NO$_x$) in the atmosphere come from:
- process of combustion by oxidation of nitrogen present in the air: the degree to which this occurs is dependent on the combustion temperature (high temperature promotes it).
- nitrogen content of the combusted materials (e.g. organic waste)
- nitric acid plant emissions

An indirect effect of acid rain, positive ion leaching out of soil can be harmful to fish in rivers and lakes. Ammonia can also enter water from the atmosphere. The surface water gets contaminated by traditional organic wastes as well as from industrial wastes.

The groundwater is contaminated by pollutants leaching through the soil. Normally, biodegradation is a natural cleaning process which is always in action. The extent to which a hazardous waste can be biodegraded depends on its half-life. Groundwater contamination is less reversible since the aerobic microbes are not present to the extent they are found in lakes and rivers.

1.3. Chemical Reactions in Major Treatment Technologies

In this section, we discuss briefly chemical reactions in the pollutant removal processes with examples of multiphase systems, which are prevalent, and provide initial guidelines for green engineering and processing. Among multiphase systems, we mention here Gas-Solid and Gas-Liquid Catalytic Reactions.

1.3.1 Gas Solid Catalytic Reactions

1. Automobile Emission Control

Catalytic converter is an anti-pollution device located between a vehicle’s engine and tailpipe. It is used to control the exhaust emission and reduce the high concentrations of hydrocarbons and carbon monoxide. Catalytic converters work by facilitating chemical reactions that convert exhaust pollutants, such as carbon monoxide and nitrogen oxides to normal atmospheric gases such as nitrogen, carbon
dioxide and water. The pollutants are reduced by contacting them with oxygen over a solid catalyst; usually an alumina supported Pt catalyst.

\[
CO + \frac{1}{2} O_2 \xrightarrow{\text{alumina supported Pt catalyst}} CO_2
\]

or

\[
HC + O_2 \xrightarrow{\text{alumina supported Pt catalyst}} CO_2 + H_2O
\]

Various types of reactors can be used and the choice will be discussed in a later chapter.

2. Catalytic Oxidation of VOCs

VOCs are a common source of pollutants present in many industrial process stack gas streams and include a variety of compounds, depending on the process industry. The catalytic oxidation removes the pollutant at \( T < T_{\text{incineration}} \), thus the capital costs are lower than that of thermal oxidation. The operating temperatures are between 600°F to 1200°F. That is around 315 to 650°C. Catalysts are bonded to ceramic honeycomb blocks so that the pressure drop through the catalytic reactor can be kept low. Design of these systems and the cost of treatment will be studied in a later chapter.

3. Incineration

Incineration, or afterburning, is a combustion process used as thermal oxidizer to remove combustible air pollutants (gases, vapors and odors) by oxidizing them. Complete oxidation of organic species results in \( CO_2 \) and \( H_2O \). Reduced inorganic species are converted to an oxidized species, e.g. the conversion of \( H_2S \) to \( SO_2 \). The presence of inorganic species, such as Cl, N, and S, in the waste stream can result in the production of acid gases after the incineration process. These acid gases, if present in high enough concentration, need to be scrubbed from the air-stream before being emitted to the atmosphere.

There are two basic types of incinerators:

*Direct thermal*: heated above the ignition temperature and held for a certain length of time to ensure complete combustion. (generally between 650 to 820 °C (1200-1500°F) for 0.3-0.5 seconds)

*Catalytic thermal*: use of lower temperature (320 to 400°C i.e. 600-750°F) at the catalyst inlet) than the direct thermal incinerators for complete combustion, and therefore use less fuel and are made of lighter construction materials.
Again the choice of technology is a balance of conflicting factors. Note that the lower fuel cost may be offset by the added cost of catalysts and the higher maintenance requirements for catalytic units. As a general rule, direct thermal units operating above \(750^\circ\) achieve higher destruction efficiencies than catalytic thermal units.

4. Selective Catalytic Reduction

Selective Catalytic Reduction (SCR) refers to reduction of a nitrous oxide to nitrogen by reacting it with ammonia in presence of a solid catalyst. Both anhydrous and aqueous ammonia have been used in actual applications.

\[
NO_x + 2 \frac{x}{3} NH_3 \rightarrow xH_2O + \left(\frac{x}{3}+1\right)N_2
\]

This technology is used for example in treating flue gases from large scale boilers.

1.3.2 Gas Liquid Reactions

Absorption is a widely used unit operation for transferring one or more gas phase inorganic species into a liquid. Absorption of a gaseous component by a liquid occurs because the liquid is not in equilibrium with the gaseous species. This difference between the actual concentration and the equilibrium concentration provides the driving force for absorption. Absorption can be physical or chemical. Several types of absorbers are used in practice, the packed tower absorber being one of the most common. Some examples are as follows:

1. FCC Off-Gas Cleaning

FCC (Fluid Catalytic Cracking) off-gas from the catalyst regenerator is a major source of pollutants in oil refineries. These gases contain \(SO_x\) (quantity depends on the sulfur content of feed) and \(NO_x\). These gases are treated in a spray column. The spray is water with additives such as alkali, caustic soda or lime. The properly designed spray column also removes particulate matter present in the off-gas as well as \(NO_x\). The pressure drop is low due to the open design of the column with few internals.

2. Wet Gas Scrubbing

This process is useful for removal of highly diluted \(SO_2\) from flue gases. The process uses a
concentrated sodium sulfite solution. The absorbed SO\textsubscript{2} is thermally released in a concentrated form from the bisulfite solution in an evaporator/crystallizer.

*Physical absorption* occurs when a soluble gaseous species, e.g. SO\textsubscript{2}, dissolves in the liquid phase, e.g. water. In the case of SO\textsubscript{2} absorbing into water, the overall physical absorption mechanism is

\[ SO_2 \text{ in Air} + H_2O(l) \leftrightarrow H_2SO_3 \leftrightarrow H^+ + HSO_3^- \leftrightarrow 2H^+ + SO_3^{2-} \]

*Chemical absorption* occurs when a chemical reaction takes place in the liquid phase to form a new species. In the case of SO\textsubscript{2} absorbing into water containing calcium, the overall absorption mechanism is

\[ SO_2 \text{ in Air} + Ca^{2+} + CO_3^{2-} + 2H_2O(l) \leftrightarrow CaSO_3 \cdot 2H_2O(s) + CO_2 \]

The absorbed SO\textsubscript{2} (in the form of bisulfite) is thermally released in an evaporator (crystallizer). SO\textsubscript{2} emerges as a concentrated gas containing 95% SO\textsubscript{2} by volume. This can be converted to elemental sulfur, liquid SO\textsubscript{2} or sulfuric acid.

3. H\textsubscript{2}S removal and spent caustic oxidation

Caustic solutions are often used to treat H\textsubscript{2}S and mercaptanes contained in gas streams. The sulfides are formed as a result of reaction with caustic solution with the sulfur bearing compounds. This waste stream is highly toxic with high chemical oxygen demand (COD). Hence, the caustic solution has to be oxidized to form thiosulfate/sulfate. The treated stream is then suitable for wastewater treatment unit.

In this chapter, we looked briefly at some reactions leading to pollution. We also consider a few methods that can be used in treatment. These treatment methods are multiphase in nature. Much research has been devoted to investigate the type of reactors that can be employed for multiphase systems and how these reactors can be improved to get better treatment. It is the purpose of this book to illustrate the principles of reaction engineering in terms of reactor design in environmental applications. In the next chapter, we will start by reviewing thermodynamic principles and applications. We will then proceed with reaction mechanisms and kinetics. We will then show how to model reaction systems. Applications to atmospheric system will be shown. Then we proceed to introduce basic reactor design models and illustrate their applications in pollution abatement and treatment.
1. **SHORT PROBLEMS (Chapter 1)**

1.1 What are the major reactions involved in smog formation?

1.2 What is the difference between “bad” ozone and “good ozone”?

1.3 Cite one example each of photochemical, biochemical and electrochemical reactions of environmental importance.

1.4 What is incremental reactivity in index?
2.1 Introduction

This chapter explains the basics of thermodynamic calculations for reacting systems. Reaction stoichiometry, heat and entropy of reaction as well as free energy are considered here. Only single phase systems are considered here. Phase equilibrium will be addressed in the next chapter. Examples and MATLAB calculations of the chemical equilibria are provided at the end of the chapter.

2.2 Reaction Stoichiometry

The principle of conservation of each atomic species applied to every well defined chemical reaction leads to reaction stoichiometry. Imagine that we have placed an invisible envelope around a finite mass of reactants and the contents of that envelope are our system in its initial state. We can count the atoms of each atomic species present in each reactant species. A chemical reaction takes place in the system. Upon reaction completion, we recount the number of each atomic species. The total number of atoms of each of the elements present in remaining reactions and products formed must remain constant. The principle of conservation of mass applied to each atomic species yields the ratio in which molecules of products are formed and molecules of reactants are reacted.

The representation of chemical species by a chemical formula indicates how many atoms of each species are there in a molecule of the species under consideration. Hence, in a molecule of carbon dioxide (CO₂), there are: one atom of carbon, C, and two atoms of oxygen, O. In a molecule of methane, CH₄, here is one atom of carbon and 4 of hydrogen, etc.

In engineering applications, a mole of the species under consideration is used rather than a chemical formula (e.g., CH₄, O₂, etc.) representing an individual molecule of a particular chemical species. One should recall that a mole is a basic unit of the amount of substance. The SI definition of a mole is: “The mole is the amount of substance of a system that contains as many elementary entities as there are carbon atoms in 0.012 kg of carbon 12.” The elementary entity (unit) may be an atom, a molecule, an ion, an electron, a photon, etc. The Avogadro’s constant is \( L = 6.023 \times 10^{23} \text{ (mol}^{-1}\text{)} \).

To obtain the number of moles of species \( j \), \( n_j \) (mol) in our system, we must divide the mass of \( j \) in the system \( m_j \) (kg), with the molecular weight of \( j \), \( M_j \) (g/mol), and multiply the result by 1000.

\[
n_j(\text{mol}) = \frac{m_j(\text{kg})}{M_j} \times 1000 = \frac{m_j(\text{g})}{M_j} \tag{1}
\]
This is equivalent to dividing the mass of the species \( j \) expressed in grams with the molecular weight, as indicated by the second equality in equation (1). So the SI mole is the same amount of substance as the “old” CGS gram mole that appears in old chemistry and physics texts.

In the US we frequently use a pound-mole (lb mol) as the measure of the amount of substance.

\[
{n_j}^* \text{(lb mol)} = \frac{m_j (lb)}{M_j} \tag{1a}
\]

It is important to note that the molecular weight of a species always has the same numerical value independent of the system of units. For example, the molecular weight of carbon is \( M_c = 12 \text{ (g/mol) = 12 (lb/lb mol) = 12 (kg/kmol)} \).

Therefore, 1 (kmol) is thousand times larger than a mole (e.g. 1 (kmol) = 10\(^3\) mol)) and 1 lbmol is 453.4 times larger than a mole, i.e. 1 (lb mol) = 453.4 moles. Accordingly, the Avogadro’s constant for a lb mole is \( L = 2.7308 \times 10^{26} \text{ (lbmole}^{-1}\text{)} \) and for a kmole is \( L = 6.023 \times 10^{26} \text{ (kmol}^{-1}\text{)} \).

To illustrate how reaction stoichiometry is developed, consider the complete combustion of methane (\( \text{CH}_4 \)) to carbon dioxide, \( \text{CO}_2 \). This is a reaction between methane, \( \text{CH}_4 \), and oxygen, \( \text{O}_2 \), that creates carbon dioxide, \( \text{CO}_2 \), and water \( \text{H}_2\text{O} \) by complete combustion.

So we have at start at end
\[
\text{CH}_4 + \text{O}_2 \quad \Rightarrow \quad \text{CO}_2 + \text{H}_2\text{O}
\]

To develop a stoichiometric equation we assume that we start with one mole of methane. This implies that one mole of carbon must be found both on the left hand side and on the right hand side of the stoichiometric equation. So, one mole of \( \text{CH}_4 \) reacted must produce one mole of \( \text{CO}_2 \). Since hydrogen is only contained in methane on the reactant side, and there are 2\( \text{H}_2 \) (two moles of hydrogen) in a mole of methane on the reactant side of the stoichiometric equation, there must be two moles of water formed on the product side in order to balance the amount of hydrogen. Now we have one mole of oxygen (\( \text{O}_2 \)) in the mole of carbon dioxide (\( \text{CO}_2 \)) on the product side and another mole of oxygen in two moles of water. Therefore, we must use two moles of oxygen on the reactant side to balance the amount of oxygen. This leads to the following stoichiometric equation for complete combustion of methane:

\[
\text{CH}_4 + 2\text{O}_2 \Leftrightarrow \text{CO}_2 + 2\text{H}_2\text{O} \tag{2}
\]

Hence, the requirement to balance out the atomic species, i.e. the application of the principle of conservation of mass of atomic species leads to the establishment of stoichiometric coefficients (multipliers that multiply the moles of various reactant and product species). The above stoichiometric
equation remains unchanged if multiplied with a common multiplier say $1/2$:

$$\frac{1}{2} CH_4 + O_2 \leftrightarrow \frac{1}{2} CO_2 + H_2O$$  \hspace{1cm} (2a)$$

or say $2$

$$2CH_4 + 4O_2 \leftrightarrow 2CO_2 + 4H_2O$$  \hspace{1cm} (2b)$$

Reaction stoichiometry, for a single reaction, such as that of equation (1) can now be represented by:

$$\sum_{j=1}^{S} \nu_j A_j = 0$$  \hspace{1cm} (3)$$

where

- $S$=total number of species in the system (e.g. 4 in case of reaction 1)
- $A_j$=chemical formula for the $j$-th species (e.g. CH$_4$, O$_2$, CO$_2$, etc.)
- $\nu_j$=stoichiometric coefficient for the $j$-th species defined as $\nu_j > 0$ for product, $\nu_j < 0$ for reactant

The stoichiometric equation satisfies the overall mass balance for the system

$$\sum_{j=1}^{S} \nu_j M_j = 0$$  \hspace{1cm} (4)$$

where $M_j$ = molecular weight of species $j$.

For example, for reaction (1) of methane combustion we have

$$\nu_{CH_4} = -1; \nu_{O_2} = -2; \nu_{CO_2} = 1; \nu_{H_2O} = 2$$

If a reaction system can be described by a single reaction, then its generalized stoichiometry is given by eq (3). Alternatively, for a single reaction between two reactants, A and B, and two products, P and S, the stoichiometry can also be represented by:

$$aA + bB = pP + sS$$  \hspace{1cm} (3a)$$

where $A$, $B$, $P$, $S$ are chemical species and $a$, $b$, $p$, $s$ are their stoichiometry coefficients, respectively. ($A = CH_4$, $B = O_2$, $P = CO_2$ and $S = H_2O$ in our example) Naturally, this implies that molecular weight of species A, B, P, S are such that equation (4) is satisfied with $\nu_A = -1$, $\nu_B = -2$, $\nu_P = 1$, $\nu_S = 2$.

This simpler form is convenient for single reactions and also in representing kinetics as discussed later. Single reaction implies that

$$\frac{\text{moles of A reacted}}{a} = \frac{\text{moles of B reacted}}{b} = \frac{\text{moles of P reacted}}{p} = \frac{\text{moles of S reacted}}{s}$$  \hspace{1cm} (3b)$$

Hence, a single reaction implies that the ratio of product produced and reactant consumed, or, a
ratio of one reactant consumed to the other reactant consumed, are constants e.g.

\[
\frac{\text{moles of } P \text{ produced}}{\text{moles of } A \text{ reacted}} = \frac{p}{a}; \quad \frac{\text{moles of } A \text{ reacted}}{\text{moles of } B \text{ reacted}} = \frac{a}{b}
\] (3c)

If that is not the case, then multiple reactions must be used to describe the system. In a generalized form this can be done as:

\[
\sum_{j=1}^{s} \nu_{ij} A_j = 0; \quad i = 1,2...R
\] (5)

where

\(\nu_{ij} = \text{stoichiometric coefficient of species } j \text{ in reaction } i\)

\(R = \text{total number of independent reactions}\)

For example, if in combustion of carbon, there is also carbon monoxide present, then two reactions are needed to describe the system. They can be as given below:

\[
2C + O_2 \leftrightarrow 2CO \quad \text{(5a)}
\]

\[
2CO + O_2 \leftrightarrow 2CO_2 \quad \text{(5b)}
\]

Here, we have a total of \(S = 4\) species (\(j = 1,2,3,4\) for \(C, O_2, CO, CO_2\), respectively), which are involved in two (\(R = 2\)) independent reactions (\(i = 1,2\)). If the above combustion reactions involve air instead of oxygen, then nitrogen is the fifth species and hence \(S = 5\), but its stoichiometric coefficient in each reaction is zero (\(\nu_{i5} = 0\)) for \(i = 1,2\) since nitrogen does not participate in these reactions. Note that the matrix of stoichiometric coefficients (for a system without nitrogen)

\[
\begin{pmatrix}
-2 & -1 & 2 & 0 \\
0 & -1 & -2 & 2
\end{pmatrix}
\]

has rank two (recall that the rank of a matrix is defined as the size of the largest nonzero determinant). Adding a third reaction

\[
C + O_2 \leftrightarrow CO_2 \quad \text{(5c)}
\]

would add a third row to the above matrix of stoichiometric coefficients, namely

\[
\begin{pmatrix}
-1 & -1 & 0 & 1
\end{pmatrix}
\]

but the rank of the matrix would remain unchanged at 2.

Clearly, eq (5c) is a linear combination (to be precise the exact sum) of (5a) and (5b). Hence, we do not have a third independent reaction, and the stoichiometry of the system can be described by any choice of two reactions of the above three reactions given by eqs. (5a), (5b) and (5c). Finding the rank of the matrix of stoichiometric coefficients will always tell how many independent reactions are needed to characterize the stoichiometry of the system. At the end of the chapter we will show how to find the rank of a matrix using MATLAB.
In summary, in any reaction system we should strive to establish the reaction stoichiometry by using the principle of conservation of elements. Then, if more than one reaction is present, the number of independent reactions can be established by determining the rank of the matrix of stoichiometric coefficients.

### 2.3 Measures of reaction progress

Let us consider first a single reaction

\[ \sum_{j=1}^{s} \nu_j A_j = 0 \]  

(3)

occurring either in a batch system (i.e. no material flow crosses the boundaries of the system during reaction) or in a continuous flow system at steady state (e.g. no variation in time). If \( n_j \) denotes the moles of species \( j \) in the batch at some time \( t \), and \( n_{jo} \) is the initial number of moles of \( j \) at time \( t_0 \), then reaction stoichiometry dictates that moles of all species can be related to their initial moles via (molar) extent of reaction \( X \).

\[ n_j = n_{jo} + \nu_j X \]  

(6a)

\((\text{moles of } j \text{ present}) = (\text{moles of } j \text{ originally present}) + (\text{moles of } j \text{ produced by reaction})\)

Moles of \( j \) produced by reaction are given by the product of the stoichiometric coefficient, \( \nu_j \), and molar extent of reaction, \( X \), which represents "moles equivalent that participated in reaction". For reactants, \( \nu_j < 0 \), and moles produced are a negative quantity, hence, they are moles reacted. For products \( \nu_j X \) is clearly a positive quantity. For a flow system at steady state,

\[ F_j = F_{jo} + \nu_j \dot{X} \]  

(6b)

where \( F_j, F_{jo} \ (\text{mol} \ j/\text{s}) \) are molar flow rate of \( j \) at exit and entrance, respectively, and \( \dot{X} \ (\text{mol} / \text{s}) \) is the molar extent of reaction.

Equation (6) indicates that in a single reaction if we can determine the change in moles of one component (say \( j = A \)), then the molar extent of reaction can be calculated \( X = (n_A - n_{Ao}) / \nu_A \). Moles of all other species \( n_j \) can now be found provided their initial moles \( n_{jo} \) were given. Equation (6) also indicates that reaction progress, i.e. its extent, is limited by the limiting reactant. The limiting reactant is the one present in amounts less than required by stoichiometry and limits the reaction extent to \( X_{max} \) where
\[ X_{\text{max}} = \left\{ \frac{n_{j_0}}{v_j} \right\} \text{smallest value over all } j \]  

(7)

Usually, the limiting reactant is denoted by \( A \) so that \( X_{\text{max}} = \frac{n_A}{v_A} \)

For multiple reactions

\[ \sum_{j=1}^{s} v_{ij} A_j = 0; \quad i = 1, 2, \ldots, R \]  

(5)

Molar extents are defined for each independent reaction \( i \) so that the moles of \( j \) are given by

\[ n_j = n_{jo} + \sum_{i=1}^{R} v_j X_i \]  

(8)

\( (\text{moles of } j \text{ present}) = (\text{moles of } j \text{ initially present}) + \sum_{\text{all reactions}} (\text{moles of } j \text{ produced by reaction } i) \)

Now, the change in moles of \( R \) species must be determined to evaluate the \( R \) extents. This involves the solution of \( R \) linear algebraic equations. Then the moles of other species can be calculated by eq (8). Maximum extents are now those that yield zero moles of one or more reactants.

Dealing with reaction stoichiometry and reaction progress results in linear algebraic equations to which all rules of linear (matrix) algebra apply. We are interested only in non-negative solutions.

Sometimes other measures of reaction progress are used, such as (molar) extent per unit volume of the system \( \xi \left( \frac{\text{mol}}{L} \right) \), which has units of concentration, or molar extent per mole which is dimensionless, or extent per unit mass. We will define them as we go along and when we need them.

Often conversion of a limiting reactant is used in single reaction systems to measure progress of reaction

\[ x_A = \frac{n_A - n_A}{n_{Ao}} \]  

(9a)

or

\[ x_A = \frac{F_A - F_A}{F_{Ao}} \]  

(9b)

The relationship between conversion and extent is readily established

\[ n_{Ao} x_A = (v_A) X \quad \text{or} \quad F_{Ao} x_A = (v_A) \dot{X} \]  

(10)

Hence, in a single reaction moles of all species can be given in terms of conversion, \( x_A \). Note that conversion is unitless while extent has units of moles, i.e., of amount of substance.
2.4 Heat of reaction

Heat of reaction is calculated as the difference between the heat of formation of products and the reactants.

\[ \Delta H_{r,i} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants}) \]  

(11)

where \( \Delta H_{r,i} \) is the heat of the reaction \( i \).

The products and reactants react proportionally to their stoichiometric coefficients. Therefore, Eqn.(11) can be written as

\[ \Delta H_{r,i} = \sum_j v_{ij} \Delta H_{f,j} \]  

(11a)

The heat of formation data is usually available of standard conditions of 298 K and 1 atm. Corresponding standard heat of reaction denoted as \( \Delta H^\circ_{r,j} \) can be calculated as

\[ \Delta H^\circ_{r,i} = \sum_j v_{ij} \Delta H^\circ_{f,j} \]  

(12)

where \( \Delta H^\circ_{f,j} \) is the heat of formation of the species \( j \) at standard conditions. Tabulated values for some species are shown in Table 1. The extensive database “chemkin” available in the public domain is another source. We will explain later how to use it.

Table 1: Heat of formation, entropy of formation, and Gibbs free energy of formation at standard conditions for selected species. State = gas, temperature, \( T=298K \) and pressure 1atm.

<table>
<thead>
<tr>
<th>Gas</th>
<th>( \Delta H^\circ J/mol )</th>
<th>( \Delta S^\circ J/molK )</th>
<th>( \Delta G^\circ =\Delta H^\circ - T\Delta S^\circ J/molK )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.0</td>
<td>-44.3557</td>
<td>0.0</td>
</tr>
<tr>
<td>Water</td>
<td>241,818</td>
<td>-228,600</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>-74,520</td>
<td>-50,832</td>
<td></td>
</tr>
<tr>
<td>Nitric oxide NO</td>
<td>90,250</td>
<td>86,686</td>
<td></td>
</tr>
<tr>
<td>Nitrogen dioxide NO2</td>
<td>33,180</td>
<td>51,961</td>
<td></td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>-110,525</td>
<td>51,961</td>
<td></td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>393,509</td>
<td>-394,355</td>
<td></td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>296,830</td>
<td>-300,139</td>
<td></td>
</tr>
<tr>
<td>Sulfur trioxide</td>
<td>-395,720</td>
<td>-370,341</td>
<td></td>
</tr>
<tr>
<td>Ozone</td>
<td>142,664</td>
<td>162,789</td>
<td></td>
</tr>
</tbody>
</table>
Group contribution methods are also available to predict these for new compounds.

Using the value of standard conditions, the value at any other condition can be calculated using “Hess Law”. This states that the enthalpy change is indifferent of the path taken as long as one lands up in the same spot. A reaction carried out at any temperature \( T \) is equivalent in terms of energy change to the sum of following three paths

(i) Cool reactants form \( T \) to \( T_{\text{ref}} \).

(ii) Carry out reaction at \( T_{\text{ref}} \) with an associated enthalpy change of \( \Delta H^\circ_{r, i} \).

(iii) Heat the products back form \( T_{\text{ref}} \) to \( T \).

The steps are schematically shown in the Figure 1.

![Figure 1. Schematics of Hess Law: Enthalpy change is indifferent of the path taken as long as one lands up in the same spot.](image)

Hence, the enthalpy change due to reaction (i.e. the heat of reaction) at temperatures different from the standard temperature can be calculated by equation (13) which adds a temperature correction term to the standard heat of reaction. This temperature correction then is the sum over all species of the algebraic product of the stoichiometric coefficients with the integral of the molar specific heat for each species from the reference (standard!) temperature to the temperature of interest.

\[
\Delta H_{r,i} = \Delta H^\circ_{r,i} + \sum_j \int_{T_{\text{ref}}}^{T} v_{ij} C_{pj} dT
\]  

(13)

The variation of \( C_p \) is usually expressed as a polynomial function of temperature

\[
C_{pi} = \sum_{\alpha=0}^{\alpha_{\text{max}}} A_{\alpha j} T^\alpha
\]  

(14a)

where \( A_{\alpha j} \) are the coefficients for species \( j \).
or
\[ C_p = A + BT + CT^2 + DT^{-2} \]  
(14b)

This is another approximate form of \( C_p \) as a function of temperature.

Up to seven constants are used in “chemkin” database (\( \alpha_{\text{max}} = 7 \)) while 4 constants are used as an approximation in many books as shown in (14b).

Substituting we find
\[ \Delta H_{i,r} = \Delta H_{i,r}^{\circ} + \nu \sum_j v_j \sum_{\alpha=0}^{a_{\text{max}}} \frac{A_{\alpha j}}{\alpha + 1} \left[ T_{\alpha+1} - \frac{T}{T_{\text{ref}}} \right] \]  
(15)

The above expression provides a method for calculation of heat of reaction at any given temperature \( T \) in an exact manner. The information needed is the heat of formation of all species at \( T_{\text{ref}} \) and the coefficients \( A_{\alpha j} \) in eq (15a) for temperature variation of molar specific heat (e.g. heat changes) \( C_p \) for each species.

2.5 **Entropy change in reaction**

\( \Delta S_r^{\circ} \) is the denoted as the entropy change of reaction at standard condition (\( T_{\text{ref}} \)) and can be calculate from the entropy of formation \( \Delta S_{f,j}^{\circ} \) for each species \( j \) participating in the reaction.

\[ \Delta S_r^{\circ} = \sum_{j=1}^s v_j \Delta S_{f,j}^{\circ} \]  
(16)

The entropy change at any other temperature \( T \) can be calculated as

\[ \Delta S_r = \Delta S_r^{\circ}(T_{\text{ref}}) + \sum_j \int_{T_{\text{ref}}}^T v_j \frac{C_{pj}}{T} dT \]  
(17)

Using the polynomial expression for \( C_{pj} \) as a function of temperature and integrating we obtain

\[ \Delta S_r = \Delta S_r^{\circ} + \sum_{j=1}^s v_j A_{0j} \ln \frac{T}{T_{\text{ref}}} + \sum_{j=1}^s v_j \sum_{\alpha=0}^{a_{\text{max}}} \frac{A_{\alpha j}}{\alpha} \left[ T^\alpha - \frac{T}{T_{\text{ref}}} \right] \]  
(18)

Knowing the entropy and enthalpy change, at any given temperature, the free energy change of reaction is calculated as:

\[ \Delta G_r = \Delta H_r - T\Delta S_r \]  
(19)

Knowledge of how \( \Delta G_r \) changes with temperature is important in determining the direction that the reaction will favor. If \( \Delta G_r < 0 \) reaction to the right or forward reaction is highly favorable, while if \( \Delta G_r > 0 \) the reverse reaction is more favorable. The temperature at which \( \Delta G_r = 0 \) is where the transition occurs. For an exothermic reaction, \( \Delta G_r \) typically increases with temperature.
Example:

i) Thermodynamic calculation for CO oxidation to CO₂. This is an exothermic reaction.

\[
\text{CO} + \frac{1}{2} \text{O}_2 \quad \xrightarrow[]{} \quad \text{CO}_2
\]

<table>
<thead>
<tr>
<th>T(K)</th>
<th>(\Delta H_r) (J/mole)</th>
<th>(\Delta S_r) (J/mole K)</th>
<th>(\Delta G_r) (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>-283,866</td>
<td>-88.55</td>
<td>-239,590.8</td>
</tr>
<tr>
<td>1500</td>
<td>-282,623</td>
<td>-86.931</td>
<td>-195,692.0</td>
</tr>
<tr>
<td>2500</td>
<td>-244,892</td>
<td>-83.71</td>
<td>-110,457</td>
</tr>
<tr>
<td>2600</td>
<td>-274,733</td>
<td>-82.33</td>
<td>-60,659</td>
</tr>
</tbody>
</table>

Reaction becomes less favorable at elevated temperature as the reaction is exothermic.

ii) Steam reforming of methane

\[
\text{CH}_4 + \text{H}_2\text{O} \quad \xrightarrow[]{} \quad \text{CO} + 3\text{H}_2
\]

This is an endothermic reaction.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>(\Delta H_r) (J/mole)</th>
<th>(\Delta S_r) (J/mole K)</th>
<th>(\Delta G_r) (J/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>215,880</td>
<td>238.2</td>
<td>96,000</td>
</tr>
<tr>
<td>700</td>
<td>222,000</td>
<td>248.3</td>
<td>35,700</td>
</tr>
<tr>
<td>900</td>
<td>224,700</td>
<td>251.3</td>
<td>-1,762</td>
</tr>
<tr>
<td>1000</td>
<td>225,660</td>
<td>252.6</td>
<td>-26,960</td>
</tr>
</tbody>
</table>

Reaction becomes favorable only at higher temperatures. This is always true for an endothermic process. Note that \(\Delta G_r\) decreases with increasing the temperature which is consistent with trend shown in Figure 2.
2.6 Chemical Thermodynamics: Brief Review of Chemical Equilibria

For simplicity consider an isothermal, single phase system subject to a single reaction.

$$\sum_{j=1}^{s} \nu_j A_j = 0$$  \hspace{1cm} (2)

The equilibrium state is then defined by the minimum in Gibbs free energy of the system \( \min \sum n_j \tilde{G}_j \) which can be expressed by

i) \( \sum_{j=1}^{s} \nu_j \tilde{G}_j = 0 \) \hspace{1cm} (20)

where

ii) \( n_j = n_{jo} + \nu_j X_e \) for all \( j \) \hspace{1cm} (21)

iii) appropriate equation of state

\( \tilde{G}_j(T, P, x_j) \) is the partial molal Gibbs free energy of \( j \) and is the function of temperature, pressure and composition. (It is often called chemical potential and denoted by \( \mu_j \))

In general

\[ \tilde{G}_j = G_j^0 + RT \ln a_j \] \hspace{1cm} (22)

where \( G_j^0 \) is the Gibbs free energy of pure species \( j \) (function of temperature only).

\( a_j \) is the activity of species \( j \);

\( n_j \) is moles of \( j \);

\( n_{jo} \) is initial moles of \( j \);

\( \nu_j \) is stoichiometric coefficient of \( j \) (positive for products, negative for reactants);

\( T \) is temperature of the system;

\( X_e \) is the equilibrium reaction molar extent;

Substitution of the second equality of equation (14) for \( \mu_j \) into equation (12) yields

\[ \sum_{j=1}^{s} \nu_j \tilde{G}_j + RT \sum_{j=1}^{s} \nu_j \ln a_j = 0 \] \hspace{1cm} (23)

Recognizing that \( \nu_j \ln a_j \) is \( \ell n a_j^{\nu_j} \) and that the sum of logarithms \( \sum_{j=1}^{s} \ell n(a_j^{\nu_j}) \) is the logarithm of the product \( \ell n \prod_{j=1}^{s} a_j^{\nu_j} \) we get the following equation
\[
\ell \prod_{j=1}^{s} a_{j}^{v_{j}} = \frac{-1}{RT} \sum_{j=1}^{s} v_{j} G_{j}^{0 - j}
\]  \hspace{2cm} (23a)

We define the standard Gibbs free energy of reaction at temperature \(T\) by

\[
\Delta G_{r} = \sum_{j=1}^{s} v_{j} G_{j}^{0}
\]  \hspace{2cm} (24)

with all \(G_{j}\) being evaluated at the temperature \(T\) of interest.

Then the thermodynamic equilibrium constant, \(K\), which is a function of temperature only, is obtained by taking the anti-logarithm of equation (23a) and is given by:

\[
K = \prod_{j=1}^{s} a_{j}^{\text{st}} = e^{\frac{\Delta G_{r}}{RT}}
\]  \hspace{2cm} (25)

where \(a_{j}\) is the activity of species \(j\).

In order to calculate the equilibrium reaction extent, \(X_{e}\), and the equilibrium composition we need to:

a) calculate \(K\) at the temperature of interest,

b) relate the activity of each species, \(j\), \(a_{j}\), to a measure of composition (e.g. mole fraction) by an appropriate model for the mixture.

c) relate the chosen measure of composition to reaction extent using stoichiometric relations indicated by ii) above.

Since the Gibbs free energy of formation is tabulated for all chemical species at \(T_{\text{ref}} = 298K\) (25°C) (or can be found from \(\Delta H\) and \(\Delta S\) data as shown in previous section) it is convenient to calculate the Gibbs free energy change due to reaction \(\Delta G_{r}^{0}\) at these standard conditions as:

\[
\Delta G_{r}^{0} = \sum_{j=1}^{s} v_{j} \Delta G_{f_{j}}
\]  \hspace{2cm} (26)

The equilibrium constant at standard temperature is then obtained from equation (25).

Van Hoff’s equation establishes the rate of change of the equilibrium constant \(K\) with temperature:

\[
\frac{d \ln K}{d T} = \frac{\Delta H_{r}}{R T^{2}}
\]  \hspace{2cm} (27)

\[
T = T_{a} (= 298 K); K_{298} = \exp(-\Delta G_{r}^{0} / R T_{0})
\]  \hspace{2cm} (28)

where \(\Delta H_{r}\) is the standard heat of reaction at temperature \(T\) (calculated as shown in previous section),
$K_{298}$ is the equilibrium constant at the standard state temperature of $T_0$ (most often 298K) and $\Delta G_{\text{rro}}$ is the standard Gibbs free energy of reaction at $T_0$ which is obtained from tabulated Gibbs free energies of formation $\Delta G_f$.

For gases (standard state pure gas at 1 atm) we use $y_j$ for mole fraction of $j$, $a_j$ is the activity of $j$, $p_j$ is partial pressure of $j$, $P$ is total pressure of the system, $\phi_j$ is the fugacity coefficient of $j$ while $\bar{f}_j$ is the partial molal fugacity of $j$.

The needed relations are included below:

\[
a_j = y_j P \left( \frac{p_j}{y_j P} \right) / 1 \text{ atm} = p_j \left( \frac{\bar{f}_j}{y_j P} \right) / 1 \text{ atm} \tag{30}
\]

\[
a_j = y_j P \phi_j / 1 \text{ atm} = p_j \phi_j / 1 \text{ atm} \tag{30a}
\]

\[
K = \prod_{j=1}^{s} a_j^\nu_j = \left( \frac{P}{1 \text{ atm}} \right)^{\sum \nu_j} \prod_{j=1}^{s} y_j^\nu_j \prod_{j=1}^{s} \phi_j^\nu_j \tag{31}
\]

\[
K = \left( \frac{P}{1 \text{ atm}} \right)^{\sum \nu_j} K_y K_\phi = \left( \frac{P}{P_0} \right)^{\sum \nu_j} K_y K_\phi \text{ where } P_0 = 1 \text{ atm.} \tag{31a}
\]

or

\[
K = \prod_{j=1}^{s} a_j^\nu_j = \prod_{j=1}^{s} p_j^\nu_j \prod_{j=1}^{s} \phi_j^\nu_j / (1 \text{ atm})^{\sum \nu_j} \tag{32}
\]

\[
K = \prod_{j=1}^{s} a_j^\nu_j = K_y K_\phi / (1 \text{ atm})^{\sum \nu_j} \tag{32a}
\]

The generalized fugacity coefficients $\phi_j, \phi_j = \left( \frac{\bar{f}_j}{y_j P} \right)$, would have to be evaluated from an appropriate equation of state. If Lewis-Randall rule is used $\phi_j = \left( \frac{\bar{f}_j}{P} \right)$.

For gases at low pressure $K_\phi \approx 1$

\[
K = \left( \frac{P}{1 \text{ atm}} \right)^{\sum \nu_j} K_y = K_y / (1 \text{ atm})^{\sum \nu_j} \tag{32b}
\]

For liquids (assuming standard state of unit activity, i.e. the standard state of each component is the pure component state) the following relations hold:

\[
a_j = x_j \gamma_j \tag{33}
\]

where $\gamma_j$ is the activity coefficient.
Since \( x_j = \frac{C_j}{C} \),
\[
K = C\sum_{j=1}^{s} \gamma_j \approx 1
\]  \hspace{1cm} \text{(35)}

For an ideal mixture, \( K_y \approx 1 \)

Above \( C_j \) is the molar concentration of species \( j \) and \( C = \sum_{j=1}^{s} C_j \) is the total molar concentration.

**Example:**

Reaction System: \( 2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3 \)

Conversion of 99% is desired

Conditions: \( T = 600^\circ\text{C} = 873^\circ\text{K} \)
\( P = 1 \) atm

Stoichiometric Feed of Pure Reactants
No Nitrogen

Calculate equilibrium conversion of \( \text{SO}_2 \) and see if 99% can be reached.

\( \Delta G_f \) and \( \Delta H_f \) for various species are given in (kcal/mol) below.

Basis: 2 moles of \( \text{SO}_2 \).

Total number of species \( S = 3 \)
\[
\sum_{j=1}^{s} \gamma_j = -1
\]
\[
n_{\text{tot}} = \sum_{j=1}^{3} n_{j,o} = 3n_{\text{tot}} = \sum_{j=1}^{3} n_j = 3 - X
\]

<table>
<thead>
<tr>
<th>Species Name</th>
<th>No.</th>
<th>Stoich. Coeff.</th>
<th>( \Delta G_f )</th>
<th>( \Delta H_f )</th>
<th>( n_{j,o} )</th>
<th>( n_j = n_{j,o} + \gamma_j X )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_2 )</td>
<td>1</td>
<td>-2</td>
<td>-71.7</td>
<td>-70.9</td>
<td>2</td>
<td>( 2 - 2X )</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>2</td>
<td>-1</td>
<td></td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( \text{SO}_3 )</td>
<td>3</td>
<td>2</td>
<td>-88.6</td>
<td>-94.4</td>
<td>0</td>
<td>( 0 + 2X )</td>
</tr>
</tbody>
</table>

Assume ideal gas mixture and write the equilibrium constant in terms of \( K_y \):
\[
K = K_y \left( \frac{P}{P_o} \right)^{\sum_{j=1}^{s} \gamma_j} = K_y \left( \frac{P}{P_o} \right)^{-1} = K_y \left( \frac{P_o}{P} \right)
\]
\[
\text{where} \hspace{1cm} (A)
\]
\[ K_y = \prod_{j=1}^{3} y_j^{y_j} = y_1^2 y_2^{-1} y_3^{+2} = \frac{y_2^3}{y_1 y_2} \left\{ \frac{y_{S0}}{y_{S0}}, \frac{2}{y_1} - 1 \right\} \]

Evaluate the mole fraction of each species in terms of reaction extent \( X \)

\[ y_1 = \frac{n_1}{n_{tot}} = \frac{2 - 2X}{3 - X} ; \quad y_2 = \frac{1 - X}{3 - X} ; \quad y_3 = \frac{2X}{3 - X} \]

Substitute these mole fractions in the expression for \( K_y \)

\[ K_y = \frac{4X^2}{3 - X)^2} = \frac{X(3 - X)}{(1 - X)^3} \]

where \( X = X_e = \) equilibrium extent

From (A)

\[ K = \frac{X^2(3 - X)(P_0)}{(1 - X)^3} \]

Calculate \( K_{298} \) at 298°K

\[ \Delta G_r = (-2)x(-71.7) + (-1)x(0) + 2x(-88.6) = -33.8 \text{kcal/mol} \]

\[ K_{298} = e^{\frac{\Delta G_r}{RT}} = e^{\frac{-33.800}{1.987 \times 298}} = e^{57.08} = 6.17 \times 10^{24} \]

Calculate \( \Delta H_r = (-2)x(-70.9) + (-1)x(0) + 2x(-94.4) = -47.0 \text{kcal/mol} \)

Assume for simplicity (in order to find a first estimate for equilibrium conditions) that \( \Delta H_r \approx const \approx \Delta H_r \)

Then

\[ \frac{d\ln K}{dT} = \frac{\Delta H_r}{RT^2} \quad ; \quad T = T_o = 298 \quad K = K_{298} \]

\[ \ln \left( \frac{K_T}{K_{298}} \right) = \frac{\Delta H_r}{R} \left( \frac{1}{298} - \frac{1}{T} \right) \]

\[ K_T = K_{298}e^{\frac{\Delta H_r}{R} \left( \frac{1}{298} - \frac{1}{T} \right)} \]

\[ K_{873} = e^{57.08 \left( \frac{47.000}{1.987 \times 298} \frac{1}{873} \right)} = e^{4.80} \]

\[ K_{873} = 121.78 \]
Note the dramatic drop in K with temperature due to the exothermicity of the reaction ($\Delta H_r < 0$). While equilibrium would have been all the way to the right at 298 K we cannot operate at such conditions because the rate is too low.

Let us see what are the equilibrium limitations at 873 K. Solve equation (B) for $K_Y$ expressed in terms of extent (see equation (C))

Solve by trial and error equation (C) for equilibrium extent $X_e = X$.

$$\frac{X^2(3-X)}{(1-X)^3} = K_{873} \left( \frac{P}{P_0} \right)$$  \hspace{1cm} (C)

where $K_{873} = 121.78; \quad \frac{P}{P_0} = 1$. Note that elevated pressure, as predicted by L’Chatelier’s principle, would help move the equilibrium to the right.

Rearrange equation (C) to use Newton-Raphson procedure

$$\phi(X) = 0 = X^2 (3-X) - 121.78 (1-X)^3$$

$$D\phi(X) = 3X(2-X) + 365.34(1-X)^2$$

$$X_{n+1} = X_n - \frac{\phi(X_n)}{D\phi(X_n)}$$  \hspace{1cm} (D)

Using a starting guess of $X_0 = 0.5$ (mol) the Newton Raphson algorithm (D) yields:

<table>
<thead>
<tr>
<th>Iteration No.</th>
<th>n = 0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent (mol)</td>
<td>0.5 0.656 0.742 0.773 0.777 0.777</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$X = X_e = 0.777$ (mol)

Conversion of $SO_2$ is:

$$x_{SO_2} = \frac{n_{SO_2,0} - n_{SO_2}}{n_{SO_2,0}} = \frac{2 - (2 - 2X)}{2} = \frac{2X}{2} = X \text{ (mol)/1 (mol)}$$

$$x_{SO_2,eq} = 0.777 << 0.99$$

Equilibrium conversion of 0.99 required by emission control cannot be reached under these conditions.

Equilibrium extent could be increased by

- lowering the temperature (but rates are lower)
- increasing the pressure (some of it can be recovered by running a turbine at the end of reactor as done in the former USSR)
2.7 Solution Thermodynamics

The equilibrium distribution of inorganic compounds in aqueous systems is of great importance in environmental engineering. These calculations are more complex than the gas phase case because of two additional considerations. (i) charge neutrality has to be maintained. (ii) system is often non-ideal. The importance of this in environmental applications is illustrated by a number of examples below.

Example 1: Heavy metals have toxicological impact and often get incorporated in biota such as fish. The free ion form $M^{++}$ for example, is often the toxic form while the complexes such as $MOH^+$, $M(OH)_2$ or ligands with $SO_4$ or other negative ions are considered to be less harmful. The distribution of the metal in various forms is a function of the total concentration and the pH of the solution. Solution thermodynamics provides us with a means of doing such calculations and helps in making judicious policy decisions.

Example 2: Consider a soil system that has some lead contamination or naturally occurring lead. The question is whether the lead is going to remain there or dissolve in ground water and enter into drinking water. The lead may remain in the solid phase depending on the pH or the presence of other ions (common ion effect described later).

Example 3: Consider $SO_2$ generated in a pollutant plume in the gas phase. This is a highly soluble gas and enters the aqueous phase with rain water. It then reacts to form various ionic species such as $HSO_3$, $SO_3^-$, $SO_4^{--}$ etc. The equilibrium distribution is important in many applications.

Example 4: Consider mercury, a highly volatile toxic metal, that is highly poisonous. Depending on the pH of the aqueous environment, mercury can be found in various forms such as $HgH$, $Hg$, $Hg^{++}$, $Hg_2^{++}$, $HgO$, $HHgO_2$ and $Hg(OH)_2$ forms. When converted to the organic form, monomethyl mercury ($CH_3Hg$) can be inserted by microorganisms, it becomes lipophyllic and gets accumulated in body fats of fish. Consumption of contaminated fish results in damage to the central nervous system, liver and kidneys and causes impaired child development. In 1950s, 200 people in Minamata Bay in Japan died from mercury poisoned fish.
2.8 Rank and checking linear independence of reactions using MATLAB

To appreciate fully what the MATLAB program does for you look first at Appendix A. In that appendix we describe the procedures involved in obtaining the rank of the matrix and identifying independent reactions.

Consider the carbon dioxide formation considered earlier. The reaction scheme is

\[
\begin{align*}
2C + O_2 & \rightleftharpoons 2CO \\
2CO + O_2 & \rightleftharpoons 2CO_2 \\
C + O_2 & \rightleftharpoons CO_2
\end{align*}
\]

(5a) (5b) (5c)

**Step 1:** type in the stoichiometric matrix as follows: Each row is reaction index and each column is the species index. Thus each row represents one reaction in the system. We take carbon, C, to be species 1, oxygen to be 2, carbon monoxide is 3, carbon dioxide is 4. Then the matrix of stoichiometric coefficients is:

\[
v = \begin{bmatrix}
-2 & -1 & 2 & 0 \\
0 & -1 & -2 & 2 \\
-1 & -1 & 0 & 1
\end{bmatrix}
\]

**Step 2:** find the rank by typing the following

```
rank(v)
```

For the above case the answer will be 2 so that there are only two independent reactions. In other words the third reaction is a linear combination of the first two reactions. To find this combination go to step 2a.

**Step 2a:** do this if the rank is less than the number of reactions.

Type

```
rref(v')
```

Note that v' is the transpose of the stoichiometric matrix and the above command reduces the tranposed matrix to the Echelon form (in this form the main diagonal of the has ones on it). The result will be

\[
\begin{bmatrix}
1.0000 & 0 & 0.5000 \\
0 & 1.0000 & 0.5000 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]
The last column gives the linear combination for the third reaction. Thus reaction (5c) is equal to 0.5 times the first reaction plus 0.5 times the second reaction. In this simple example it is obvious by inspection as well.

**Step 3:** To find the system invariants (these will be relations between moles produces or consumed among various species), type

rref(v)

This reduces the stoichiometric matrix to the echelon form. The result for our example is:

<table>
<thead>
<tr>
<th>1</th>
<th>0</th>
<th>-2</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>2</td>
<td>-2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The last two columns here provide the invariants. Thus

\[ \Delta F_3 = -2 \times \Delta F_1 + 2 \times \Delta F_2 \]

and

\[ \Delta F_4 = 1 \times \Delta F_1 - 2 \times \Delta F_2 \]

Here \( \Delta F \) represents the change in molar flow rate between the exit and entrance for species \( I \).

Note that the last row is all zero indicating that the third reaction is redundant and does not contribute to the invariant. (recall that the rank was two).

Let us see what the implication of all this is; the above equations tell us that only two values \( \Delta F_1 \) and \( \Delta F_2 \) are independent. For example, in an experiment suppose we find that 5 mole/sec of carbon has reacted.

Then \( \Delta F_1 = -5 \).

We also find that 4 mole/sec of oxygen is consumed.

\( \Delta F_2 = -4 \).

Then using the equations above we find

\[ \Delta F_3 = (-2)(-5) + (2)(-4) = 2 \text{ mole/sec is the amount of CO formed.} \]

Also

\[ \Delta F_4 = (1)(-5) - (2)(-4) = 3 \text{ mole/sec of } CO_2 \text{ is formed.} \]
If the measurements show otherwise, then either the measurements are in error or some other C bearing species is being formed (not likely here). Hence in this case the measurements would be in error. Thus, the invariants of a reaction are useful in proper bookkeeping of the various species.

2.9 MATLAB PROGRAM FOR CALCULATION OF EQUILIBRIUM COMPOSITION OF A REACTING GAS MIXTURE

The following program calculates the equilibrium composition of a gas mixture. The program is written for the SO$_2$ example and can be modified easily for other cases. The best way to learn this is for the students to TYPE out the program as it is and execute it on matlab. This way they get familiar with the programming as well. The program also illustrates the use of the solver FSOLVE to solve a set of non-linear algebraic equations. The program is interspaced with some explanation and these statements need to be omitted in the actual program.

PREAMBLE SECTION

% filename gaseq; created on jan 31-03 by P.A.Ramachandran.
% computes the equilibrium composition of a reacting mixture.

% preamble
   global ng ns nr tempin prin prctot xg nu ...
   global keq298 keq delhr
   global rgas
   global n ntot

At this part of the program the number of gas phase species ng and number of reactions nr are to be entered.

% number of species and number of reactions
   ng = 3;
   nr = 1;

DIMENSIONING THE VECTORS

This is required but no action by user is needed.

% initialize the vectors.
   keq298 = zeros(nr, 1);
   keq = zeros(nr, 1);
delhr = zeros(nr, 1);
xg = zeros(ng,1);
nu = zeros ( nr, ng);
zeta = zeros(nr,1) ;

**USER DATA SECTION**

**A: REACTIONS**
Here the reaction specific variables are entered
These are the stoichiometric matrices and the equilibrium constants for each reaction at 298K and the heat of reaction at 298K. The program assumes that the heat of reaction is independent of temperature. Note that the gas constant $r_{gas}$ must have consistent unit with the heat of reaction.

% provide values for stoichimetry and eq constants.
nu(1,1) = -2. ;
nu(1,2) = -1.
nu(1,3) = 2. ;
keq298(1) = 6.1593E+24 ;
delhr(1) = -47000.0  ; %assumed constant (not a function of T)
$rgas = 1.97$ ;  % gas constant; use consistent units

**B: PROCESS CONDITIONS**
Here the temperature, pressure and the moles of each species present in the initial mixture are specified. The user must provide a guess value for the extent of reaction (zeta vector). Try to provide realistic values, for example the conversion of a key component can not be greater than one. This will fix the maximum value for zeta

% provide the feed conditions.
tempin = 873.0;
prin = 1.0e+05;
% initial moles.
xg(1) = 2.0;
xg(2) = 1.0;
xg(3) = 0.0;
% provide initial values for extent of reactions
zeta(1) = 0.4

**CALCULATION SECTION**
At this stage the matalb takes care of the rest of the calculations
% mtlab function fsolve solver is called to find the roots
% the required equations are programmed in a file fun_eq.m
zeta = fsolve ( 'fun_eq', zeta)
% post process the results.
% molar flow rates at exit = TYPE n
% total moles = TYPE ntot

Post processing can be done by typing n which gives the moles of species at Equilibrium,. The conversion and other required information can be calculated easily on the matlab command window.

**FUNCTION SUBROUTINE**
The program requires a function subroutine which calculates the function to be solved. The subroutine is in a file fun_eq.m and the listing is shown below. No changes in this by user is needed. Students may want to study how this is written by following this with the text earlier.

```
function fvec = fun_eq( zeta)
% filename fun_eq; created on jan 31-03 by P.A.Ramachandran.
% Defines the (nr) functions to be solved.

% preamble
  global ng ns nr tempin prin ctot xg nu ...
  global keq298 keq delhr
  global n ntot
  global rgas
  fvec = zeros ( nr,1) ;

  ptotatm = prin /1.0e+05 ;
```
% find K at the desired conditions
for i = 1: nr
    keq(i)=keq298(i)*exp( delhr(i) /rgas *(1./298-1./tempin)) ;
end

% number of moles of each species for the given extents
% nj0 = 1 for these calculations
for j = 1: ng
    n(j) = xg(j);
    for i=1:nr
        n(j) = n(j) + nu(i,j) * zeta(i);
    end
end

% find ntot
ntot = 0.0;
for j = 1: ng
    ntot = ntot + n(j);
end

% find the mole fractions for each species
pp = n /ntot * ptotatm;

% set up discrepancy function for each reaction
for i = 1: nr
    prod = 1.0;
    for j = 1: ng
        prod = prod * pp(j)^nu(i,j);
    end
    fvec(i) = keq(i) - prod
end

----------------------------------

The students should run the program for other cases for example to study the effect of inerts, like nitrogen, pressure or other systems involving multiple reactions.

We will now illustrate use of this program for a combustion application.
Example: Chemical equilibrium sets an upper limit on the composition of combustion gases. Given a mixture of CO, CO$_2$ and O$_2$ we need to find the CO concentration as a function of exhaust gas temperature. Once CO$_2$ is formed, it is unlikely that CO will be formed as the gas cools since the reaction rates are slowed down. Hence the maximum CO in the exhaust gas can be found from the equilibrium calculations.

As an example, consider an exhaust gas mixture with 18%CO$_2$, 3.3%O$_2$ and the rest N$_2$. Temperature of this gas is raised to 1600K. Find the equilibrium composition of this gas assuming the reaction

$$\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$$

We run the program with 4 species the fourth being inert (N$_2$).

The sample results are as follows:

***** COMPUTED RESULTS **********
Equilibrium constant of reaction 1 is 1.9643907E-05
Heat of reaction 1 is 279958.6 (J/mol)
Free energy change of reaction 1 is 144168.0 (J/mol)
Program converged
The extent of reaction 1 is 1.9459629E-03 (mole)

We use 100 moles total as the input conditions. Moles of CO in the exhaust gas is therefore 1.955E-03% of the total mole or 19.5 ppm (by moles or volume).

Problem for discussion
Predict the effect of temperature (range of 1000 to 2000K) on the CO content of exhaust gas and plot the results. If CO reduction was the only goal, would you operate at high temperature or low temperature?

Example: Consider a gas to be 3.3%O$_2$ and rest N$_2$. This presumably simulates an exhaust gas from an internal combustion engine. The following reactions take place

$$N_2 + O_2 \rightleftharpoons 2NO$$
$$NO + 1/2O_2 \rightleftharpoons NO_2$$

Find the concentrations of NO and NO$_2$ at 1800K and 1 atm.
Again we use the fortran program since all these gases are in the chmkin database. We modify the datafile and run the program to find the following results.

Equilibrium constant of reaction 1 is 1.1928983E-04
Heat of reaction 1 is 181059.9 (J/mole)
Free energy change of reaction 1 is 135194.9
Equilibrium constant of reaction 2 is 5.1639900E-03
Heat of reaction 2 is -57594.48 (J/mole)
Free energy change of reaction 2 is 78807.43 (J/mole)
Program converged

The extent of reaction 1 is 8.5949510E-02 (J/mole)
The extent of reaction 2 is 1.7736210E-04 (J/mole)

NO formed = 2 \( x_1 - x_2 \)
N\(_2\)O Formed = \( x_2 \)

The above are percentages since the total starting moles are assumed as 100. Hence the gas has 172ppm of NO and 1.77 ppm of NO\(_2\)

### 2.10 STUDY QUESTIONS

What is the significance of the rank of the stoichiometric matrix?

State the measure of progress of reactions for multiple reactions.

How does the equilibrium constant vary with temperature?

How is \( K_{eq} \) and \( K_y \) related to each other? Show one example?
2.11 EXERCISES

2.1 The principle of conservation of elements must be applied in order to obtain the stoichiometric coefficients in a single reaction. Assume that there are S chemical species that are either products or reactants in the reaction and there are N elements present as constituents. Let the number of atoms of element i in species j be $v_j^i$. Let the yet unknown stoichiometric coefficient of species j be $u_j$. Show that the conservation principle above requires $\sum_{j=1}^{S} u_j v_j^i = 0$ for all $i = 1, 2, N$. Apply this to the reaction of complete combustion of methane and show how to determine the unknown $u_j$'s.

2.2 In a reaction system consisting of methane, oxygen, carbon monoxide, water, hydrogen and carbon monoxide, the following 6 reactions ($R' = 6$) may occur:

- $\text{CH}_4 + \frac{3}{2} \text{O}_2 = \text{CO} + 2\text{H}_2\text{O}$ (1)
- $\text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2$ (2)
- $\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}$ (3)
- $\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$ (4)
- $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ (5)
- $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$ (6)

Find the number of independent reactions $R$.

2.3 Carbon (10 moles initially) is burned with oxygen. At the end of reaction 4 moles of carbon are left and 4 moles of CO are produced. The produced amount of $\text{CO}_2$ is unknown.

(i) Write the stoichiometric matrix with carbon and CO as components (1) and (2)

(ii) Find the matrix in echelon form.

(iii) Find the moles of $\text{O}_2$ consumed and $\text{CO}_2$ produced in the process.

2.4 The equilibrium constant for

$$\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2} \text{O}_2$$

at 1000 K is $6.0462 \times 10^{-11}$.

Find the value at 2600 K if the heat of reaction is 282 kj/mole.

2.5 Find the thermodynamic data for the reaction

$$\text{NO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NO}_2$$
Using a suitable database (report which one you used) over a temperature range of 500 to 2500 K, determine at what temperature would you expect a larger NO\textsubscript{2} concentration. Low or high? What is the equilibrium composition.

2.6 What is the effect of pressure on CO formation in a combustion system? At 2600 K, find the CO contents of the exhaust gas if the pressure were 2 atm. Initial composition is the same 18% CO\textsubscript{2}, 3.3% O\textsubscript{2}, 78.7% N\textsubscript{2}. As in the Matlab program example.

2.7 Propane is burned in air with 1.25 times the stoichiometric air. Find the composition of exhaust gases assuming that only CO\textsubscript{2} and H\textsubscript{2}O are formed.

2.8 For the composition in Question (2.7) find the equilibrium composition of CO if the combustion takes place at 1800 K and 1 atm pressure.

2.9 Find the equilibrium composition for the above case using the net program.
APPENDIX 1A.

In case of multiple reactions it is important to find the number of independent reactions. This determines for how many species the change in the number of moles may occur independently, i.e., for how many species we must monitor the change in the number of moles caused by reactions in order to compute the composition of the whole system (i.e., to compute the changes in the number of moles of all other species).

Usually the problem is stated as $R^1$ reactions between $S$ species:

$$\sum_{j}^{S}v_{ij}A_j = 0; \quad i = 1, 2, \ldots, R^1$$

where $v_{ij}$ is the stoichiometric coefficient of species $j$ in reaction $i$ (Recall $v_{ij} > 0$ products, $v_{ij} < 0$ reactants). Then:

a) Find the number of independent reactions $R \leq R^1$.

b) Find the molar extents of the $R$ independent reactions $(\dot{X}_i, i = 1, \ldots, R)$ in terms of the measured changes in the number of moles, $\Delta F_j$, of $R$ key species.

$$\left(\Delta F_j = F_j - F_{jo}, j = 1, 2, \ldots, R\right)$$

c) Express the changes in moles of the remaining $S - R$ species, $(\Delta F_j, j = R + 1, R + 2, \ldots, S)$ in terms of changes in moles of the selected $R$ key species.

d) Determine the extents of the remaining $R^1 - R$ (dependent) reactions in terms of the calculated $R$ extents (if so desired).

First we will introduce the classical procedure and then show a short-cut method which accomplishes all of the above in a single step.
Classical Method:

Consider the matrix of stoichiometric coefficients of all original $R^l$ reaction equations and $S$ species (i.e., the $(R' \times S)$ matrix):

\[
\mathbf{v}_{\text{original}} = \begin{pmatrix}
v_{11} & v_{12} & \cdots & v_{1S} \\
v_{21} & v_{22} & \cdots & v_{2S} \\
v_{R1} & v_{R2} & \cdots & v_{RS}
\end{pmatrix}
\]

and find its rank, i.e., the largest nonzero determinant. Use for example Gaussian elimination (see for example E. Kreyszig "Advanced Engineering Mathematics" Fourth Edition, Wiley, N.Y. 1979, Chapter 7-6). This procedure will generate $R^l - R$ rows of zeros when $R$ is the rank of the matrix and the number of independent reactions.

All reactions for which rows of zeros are generated are the dependent ones. The rest is picked as a set of $R$ independent reactions for which the matrix of stoichiometric coefficients is:

\[
\mathbf{v} = \mathbf{v}_{\text{new}} = \begin{pmatrix}
v_{11} & v_{12} & \cdots & v_{1R} \\
v_{21} & v_{22} & \cdots & v_{2R} \\
\vdots & \vdots & \ddots & \vdots \\
v_{R1} & v_{R2} & \cdots & v_{RR}
\end{pmatrix}
\]

Please understand that reactions have now been renumbered, since some were deleted as being dependent, and the elements of the new matrix of stoichiometric coefficients $\mathbf{v}$ do not necessarily correspond in order one to one to the elements of the old matrix.

Now using the law of stoichiometry we can write:

\[
\frac{\Delta F}{(Rx1)} = \mathbf{v}^T \cdot \mathbf{X}
\]

\[
\left(\begin{array}{c}
\frac{\Delta F}{(Rx1)} \\
\mathbf{X}
\end{array}\right) = \left(\begin{array}{c}
\mathbf{v}^T \\
\mathbf{X}
\end{array}\right)
\]

where $\mathbf{v}^T$ is the transpose of the matrix $\mathbf{v}$ i.e., is matrix $\mathbf{v}$ with columns and rows interchanged.
Expanded view of eq (1) is:

\[
\begin{pmatrix}
\Delta F_1 \\
\Delta F_2 \\
\vdots \\
\Delta F_j \\
\vdots \\
\Delta F_R
\end{pmatrix}
\begin{pmatrix}
v_{1j} v_{2j} \ldots v_{Rj}
\end{pmatrix}
\begin{pmatrix}
\dot{X}_1 \\
\dot{X}_2 \\
\vdots \\
\dot{X}_j \\
\vdots \\
\dot{X}_R
\end{pmatrix}
\]

(1a)

Considering now just the \( j \)-th row of the vector \( \Delta F \), and remembering that matrix multiplication is rows into columns, we get:

\[
\Delta F_j = v_{1j} \dot{X}_1 + v_{2j} \dot{X}_2 + \ldots + v_{Rj} \dot{X}_R
\]

(1b)

We can solve equation (1) and we will show a formal solution in terms of Cramer's rule. (This of course is not practical and actual solution should proceed by Gaussian elimination or Gauss Jordan technique). The solution of (1) is:

\[
\dot{X} = \left( v^T \right)^{-1} \Delta F
\]

(2)

where \( \left( v^T \right)^{-1} \) is the inverse matrix of \( v^T \)[see Kreyszig or some other linear algebra text to find how to obtain it by Gauss Jordan technique].

Since the value of the determinant is unchanged if rows and columns are interchanged, the solution in terms of Cramer's rule is:

\[
\dot{X}_j = \frac{\det(v)_{j\Delta F}}{\det(v)} \quad j = 1,2,\ldots,R
\]

(3)
where

$$\text{det}(\mathbf{v}) = \begin{vmatrix} v_{11} & v_{12} & \cdots & v_{1R} \\ v_{21} & v_{22} & \cdots & v_{2R} \\ \vdots & \vdots & \ddots & \vdots \\ v_{i1} & v_{i2} & \cdots & v_{iR} \\ \vdots & \vdots & \ddots & \vdots \\ v_{R1} & v_{R2} & \cdots & v_{RR} \end{vmatrix}$$

and $\text{det}(\mathbf{v})_{i\Delta F}$ is the $\text{det}(\mathbf{v})$ where the $i$-th row is replaced by $\Delta F$, $\Delta F_i$, etc.

$$\text{det}(\mathbf{v})_{i\Delta F} = \begin{vmatrix} v_{11} & v_{12} & \cdots & v_{1R} \\ v_{21} & v_{22} & \cdots & v_{2R} \\ \vdots & \vdots & \ddots & \vdots \\ \Delta F_1 & \Delta F_2 & \cdots & \Delta F_R \\ \vdots & \vdots & \ddots & \vdots \\ v_{R1} & v_{R2} & \cdots & v_{RR} \end{vmatrix}$$

This solves parts (a), of finding the number of independent reactions and (b), of relating extents of independent reactions to measured changes in moles of key species. We have related $R$ extents, $X_i$, to the changes in moles of $R$ species, $\Delta F_i, i=1,2,\ldots,R$.

If $R < S$ we need to express the changes in moles of the remaining $S-R$ species in terms of the changes in moles of the first $R$ species (part c).

Stoichiometry dictates that eq (1b) is valid for all species, not just for the first $R$ species for which we have used it so far. Hence, we can write

$$\Delta F_k = \sum_{i=1}^{R} v_{ik} \Delta X_i, k = R+1, R+2,\ldots,S$$

This gives the change in moles of the remaining $S-R$ species in terms of the now known $R$ extents. We can proceed a step further and substitute equation (3) into equation (6) to obtain:

$$\Delta F_k = \sum_{i=1}^{R} v_{ik} \frac{\text{det}(\mathbf{v})_{i\Delta F}}{\text{det}(\mathbf{v})}$$
After rearrangement we recognize the following:

\[ 0 = \Delta F_k \det(v) - \sum_{i=1}^{R} v_{ik} \frac{\det(v)_{ik}}{\det(v)} (-1)^{k+1} \]

The left hand side of the above equation is just an expansion in minors of the determinant on the right hand side when the expansion is done about the elements of the last \((R + 1)\) column. If we develop this determinant with respect to the first row (the value of the determinant is properly zero indicating that \(\Delta F_k, k = R + 1, R + 2, \ldots, S\) is linearly dependent on the first \(R\Delta F_j's\) ) we get:

\[ \Delta F_k \det(v) - \sum_{i=1}^{R} \det(v)_{ik} \Delta F_i = 0 \]

which finally yields \(\Delta F_k\) in terms of the first \(R\) \(\Delta F_i's\):

\[ \Delta F_k = \sum_{i=1}^{R} \det(v)_{ik} \Delta F_i, k = R + 1, \ldots, S \]

where \(\det(v)_{ik}\) is \(\det(v)\) with the \(i\)-th column replaced by \(v_{1k}, v_{2k}, \ldots, v_{Rk}\).

Note that in proving eq (8) and (9) one uses the property that the value of a determinant must be multiplied by \((-1)\) each time two rows or two columns are interchanged.

Our results can be summarized as follows: The \(R\) extents are obtained from eq (3) which now becomes

\[ \dot{X}_i = \frac{\det(v)_{ij}^{AE}}{\det(v)} = \sum_{j=1}^{R} (-1)^{i+j} \frac{\det(v)_{ij}^{AE}}{\det(v)} \Delta F_j, i = 1, 2, \ldots, R(3a) \]

\(\det(v)_{ij}^{AE}\) is \(\det(v)\) with row \(i\) and column \(j\) deleted. The change in moles for the non-key species is given by:
\[
\Delta F_k = \sum_{i=1}^{r} \frac{\text{det}(v_i)}{\text{det}(v)} \Delta F^i; \quad k = R + 1, R + 2 \ldots S
\]  

(10)

**Shortcut Method:**

This method gives all the information in one single sweep. Consider the augmented matrix

\[
\begin{pmatrix}
v^T & \Delta F \\
\text{original} & \text{dim} \end{pmatrix}
\]

Use Gauss-Jordan technique on this augmented matrix to generate 1’s on the diagonal and zeros elsewhere by normalizing the pivot element and by generating \( v^i_j \leftarrow v^i_j - v^i_k v^k_j \).

The procedure stops when we cannot generate any more 1's on the diagonal and the rows below the last 1 are filled with zeros. Remember, we can always interchange rows, keeping track to renumber our reactions accordingly, to get the rows with zeros on the bottom. When we are finished with the Gauss-Jordan procedure the augmented matrix has the form:
In the upper left hand corner the \((R \times R)\) matrix with 1's on the diagonal and zeros everywhere else determines the rank \(R\) and the number of independent reactions.

The first \(R\) rows on the top in the right hand corner, to the right of the partition, give the \(R\) extents:

\[
\dot{X}_i = \sum_{j=1}^{R} \alpha_{ij} \Delta F_j; i = 1, 2, \ldots R
\]

(11)

where \(\alpha_{ij}\) have been determined by the procedure. By comparison with eq (3a) we see that the \(\alpha_{ij}\) generated by the procedure must be

\[
\alpha_{ij} = (-1)^{i+j} \frac{\det\{v_i X_j\}}{\det\{v\}}; i = 1, 2, \ldots, R; j = 1, 2, \ldots, R
\]
The lower right corner, i.e. the last $S - R$ rows to the right of the partition, defines the $(S - R)$ invariants of the system:

$$\Delta F_k + \sum_{j=1}^{R} \beta_{kj} \Delta F_j = 0; k = R + 1, R + 2, \ldots, S$$

(12)

These linear combinations of $\Delta F_j$'s (invariants) must be zero. Otherwise the last $S - R$ rows would not have a $0 = 0$ relation and the system would be impossible and have no solution, meaning that a mass balance was violated with a wrong stoichiometric coefficient somewhere.

Comparison of equation (12) and equation (10) gives:

$$\beta_{kj} = -\frac{\det(y)}{\det(y)}; k = R + 1, R + 2, \ldots, S; j = 1,1,\ldots, R$$

(13)

Note that $\beta_{kj}$ have been calculated by the Gauss-Jordan procedure.

Finally, the $(R \times (R^1 - R))$ matrix of $\lambda^s$, squeezed between the diagonal $(R \times R)$ identity matrix and the partition, yields the coefficients for expressing the extents of dependent reactions in terms of the independent ones:

$$\dot{X}_k = \sum_{i=1}^{R} \lambda_{ki} \dot{X}_i; k = R + 1, R + 2, \ldots, R^1$$

(14)

Let us document this by an example:

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>(C)</th>
<th>(O_2)</th>
<th>(CO)</th>
<th>(CO_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R^1) = 3</td>
<td>(2C) + (O_2) = (2CO)</td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
</tr>
<tr>
<td>(S = 4)</td>
<td>(2CO) + (O_2) = (2CO_2)</td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>(C) + (O_2) = (CO_2)</td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
</tr>
</tbody>
</table>

$$\Psi_{original} = \begin{pmatrix} -2 & -1 & 2 & 0 \\ 0 & -1 & -2 & 2 \\ -1 & -1 & 0 & 1 \end{pmatrix}$$
Use short-cut method. Write the transpose matrix:

\[
\mathbf{v}_{\text{original}}^T = \begin{pmatrix}
-2 & 0 & -1 \\
-1 & -1 & -1 \\
2 & -2 & 0 \\
0 & 2 & 1
\end{pmatrix}
\]

Then proceed with the augmented matrix \((\mathbf{v}_{\text{original}}^T \Delta F)\) as follows:

\[
\begin{pmatrix}
-2 & 0 & -1 & \Delta F_1 \\
-1 & -1 & -1 & \Delta F_2 \\
2 & -2 & 0 & \Delta F_3 \\
0 & 2 & 1 & \Delta F_4
\end{pmatrix}
= \begin{pmatrix}
1 & 0 & \psi/2 & -\Delta F_1/2 \\
0 & -1 & -1/2 & +\Delta F_2 - \Delta F_1/2 \\
0 & -2 & -1 & \Delta F_3 + \Delta F_1 \\
0 & 2 & 1 & \Delta F_4
\end{pmatrix}
\]

\[
\begin{aligned}
R &= 2 \\
S - R &= 2 \begin{pmatrix}
1/2 & -\Delta F_1/2 \\
0 & \Delta F_1/2 - \Delta F_2 \\
0 & 2\Delta F_1 - 2\Delta F_2 + \Delta F_3 \\
0 & -\Delta F_1 + 2\Delta F_2 + \Delta F_4
\end{pmatrix}
\end{aligned}
\]

There are 2 (two) independent reactions. Their extents in terms of molar changes of the first two species are:

\[
\begin{aligned}
\mathbf{x}_1 &= -\frac{1}{2} \Delta F_1 = -\frac{1}{2} (F_1 - F_{10}) = \frac{1}{2} (F_{10} - F_1) \\
\mathbf{x}_2 &= \frac{1}{2} \Delta F_1 - \Delta F_2 = (F_{20} - F_2) + \frac{1}{2} (F_{10} - F_1)
\end{aligned}
\]

There are \(R = 2\) independent reactions and their extents are given above.

There are \(S - R = 4 - 2 = 2\) two invariants.

The changes in the number of moles of species 3 and 4 can be expressed in terms of the change in moles of species 1 and 2 using the two invariants as shown below:

\[
\begin{aligned}
\Delta F_3 &= 2(\Delta F_2 - \Delta F_1) = 2(F_2 - F_{20} - F_1 + F_{10}) \\
\Delta F_4 &= \Delta F_1 - 2\Delta F_2 = 2(F_{20} - F_2) - (F_{10} - F_1)
\end{aligned}
\]
The extent of the third reaction is:

\[ \text{extent of the dependent reaction } \left\{ \dot{x}_3 = \frac{1}{2} \dot{x}_1 + \frac{1}{2} \dot{x}_2 \right\} \]

i.e. the third reaction is the sum of the first two divided by two. This in this simple case is obvious by inspection.

Check the classical method results. By this method we would have first determined \( R = 2 \) and would have taken the first two reactions as independent. The \( R \times R = 2 \times 2 \) matrix of stoichiometric coefficients using the first two components as the key ones, is:

\[
\begin{pmatrix}
-2 & -1 \\
0 & -1
\end{pmatrix}
\]

\[ \text{det}(\mathbf{v}) = \begin{vmatrix} -2 & -1 \\ 0 & -1 \end{vmatrix} = 2 \]

\[ \text{det}(\mathbf{v}_{x1}) = \text{det}(-1) = -1 \quad \text{det}(\mathbf{v}_{x2}) = \text{det}(0) = 0 \]

\[ \alpha_{11} = (-1)^2 \frac{-1}{2} = -\frac{1}{2} \quad \alpha_{12} = (-1)^3 \frac{0}{2} = 0 \]

\[ \alpha_{21} = (-1)^3 \frac{-1}{2} = \frac{1}{2} \quad \alpha_{22} = (-1)^3 \frac{-2}{2} = -1 \]

Hence:

\[ \dot{x}_1 = -\frac{1}{2} \Delta F_1 + 0 \Delta F_2 \quad \dot{x}_2 = \frac{1}{2} \Delta F_1 - \Delta F_2 \quad QED \]

checks

Now:

\[ \begin{pmatrix}
2 & -1 \\
-2 & -1
\end{pmatrix}
\]

\[ \frac{2}{2} = 2 \quad \beta_{31} = -\frac{2}{2} = 2 \]

\[ \begin{pmatrix}
-2 & 2 \\
0 & -2
\end{pmatrix}
\]

\[ \frac{-2}{2} = -2 \quad \beta_{32} = -\frac{0}{2} = 2 \]

\[ \Delta F_3 + 2 \Delta F_1 - 2 \Delta F_2 = 0; \quad \Delta F_4 - \Delta F_1 + 2 \Delta F_2 = 0 \quad \text{checks} \]

Once we know the number of independent reactions and their extents we can write for all species \( j = 1, 2, \ldots, S \)
\[ F_j = F_{j0} + \sum_{i=1}^{R} \nu_{ij} \Delta_i; \quad i = 1, 2, \ldots, R \]  

(15)

\[ F_{\text{tot}} = \sum_{j=1}^{S} F_j = F_{\text{tot},o} + \sum_{i=1}^{R} \bar{\nu}_i \Delta_i; \quad \bar{\nu}_i = \sum_{j=1}^{S} \nu_{ij} \]  

(16)

Another Shortcut Method:

Another approach to the above problem is to count all the chemical elements present in the reaction system under consideration (say total number of elements is \( E \)) and form the matrix of coefficients \( \Psi^E \) so that \( \nu_{ij} \) is the number of atomic species \( i \) present in the chemical species \( j \). The matrix \( \Psi^E \) is a (EXS) matrix. One should find the rank of matrix \( \Psi^E \), say \( R^E \). Then the number of independent reactions is equal to the total number of chemical species minus the rank of the matrix \( \Psi^E \), i.e.,

\[ R = S - R^E \]  

(17)
APPENDIX 1B

RELATIONSHIPS BETWEEN MEASURES OF COMPOSITION AND REACTION EXTENTS

Ideal Gas Mixture:

Equation of State:

\[ C_{\text{tot}} = \frac{P}{RT}; \quad C_{\text{tot,o}} = \frac{P_o}{RT_o} \]

Define \( \frac{X_i}{F_{\text{tot,o}}} = x_i \) extent of reaction \( i \) per mole or original mixture

total molar flow rate:

\[ F_{\text{tot}} = F_{\text{tot,o}} \left[ 1 + \sum_{i=1}^{R} \bar{v}_i x_i \right] \]

volumetric flow rate:

\[ Q = Q_o \frac{P T_o}{P T} \left( 1 + \sum_{i=1}^{R} \bar{v}_i x_i \right) \]

molar concentration:

\[ C_j = C_{\text{tot,o}} \frac{P T_o}{P_o T} \frac{y_j + \sum_{i=1}^{R} \bar{v}_i x_i}{1 + \sum_{i=1}^{R} \bar{v}_i x_i} \]

\( \bar{v}_i = \sum_{j=1}^{S} v_{ij} \)

total molar concentration:

\[ C_{\text{tot}} = C_{\text{tot,o}} \frac{P T_o}{P_o T} = \frac{P}{RT}; \quad C_{\text{tot,o}} = \frac{P_o}{RT_o} \]

mole fraction:

\[ y_j = \frac{y_j M_j}{\sum_{j=1}^{R} y_j M_j} = \frac{y_j M_j}{\sum_{j=1}^{R} y_j M_j} \]

mass fraction:

\[ w_j = \frac{w_{j} M_j}{\sum_{j=1}^{R} w_{j} M_j} = w_{j} + \sum_{i=1}^{R} \bar{v}_i M_j \xi_i \]

molar extent per unit mass:

\[ \xi_i = \frac{X_i}{n_{\text{tot}}} = \frac{X_i}{\sum_{j=1}^{S} F_j M_j} \]
Note: Mass fractions are linearly related to molar extents per unit mass. This prompts some investigators to express rate forms for gas reactions in terms of mass fractions. Unfortunately, the fundamental driving force for the rate is concentration. Thus this approach is limited to a narrow range of conditions.

Notations:

\[
F = \text{molar flow rate (mol/s)}; \quad \dot{X} = \text{molar extent (mol/s)}
\]

\[
\dot{n}_\text{tot} = \text{mass flow rate (g/s)}; \quad M_j = \text{molecular weight}
\]

For liquids (\(\rho \approx \text{const}\)):

- total molar flow rate:
  \[
  F_{\text{tot}} = F_{\text{tot},o}\left[1 + \sum_{i=1}^{R} \xi_i \dot{X}_i\right]
  \]

- volumetric flow rate:
  \[
  Q = Q_o
  \]

- molar concentration:
  \[
  C_j = C_{jo} + \sum_{j=1}^{R} \nu_j \xi_j; \quad \xi_j = \frac{\dot{X}_j}{Q}
  \]

- mole fraction:
  \[
  y_j = \frac{y_{jo} + \sum_{j=1}^{R} \nu_j x_i}{1 + \sum_{j=1}^{R} \nu_j x_i}
  \]

- mass fraction:
  \[
  w_j = \frac{y_j M_j}{\sum_{j=1}^{R} y_j M_j} = W_{jo} + \sum_{j=1}^{R} \nu_j M_j \xi_j
  \]

Define types of yield for multiple reactions.

Point yield of species \(P\) with respect to reactant \(A\) :

\[
y\left(\frac{P}{A}\right) = \frac{R_P}{-R_A}
\]

Overall (Relative) yield of \(P\) with respect to reactant \(A\) :
\[
Y \left( \frac{P}{A} \right) = \frac{F_p - F_{po}}{F_{Ao} - F_A}
\]

Overall operational yield:

\[
Y \left( \frac{P}{A} \right) = \frac{F_p - F_{po}}{F_{Ao}} = \frac{Y}{x_A}
\]

\[\uparrow \text{conversion of } A.\]
PHASE EQUILIBRIA

(CHE 505)

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CHAPTER 3: PHASE EQUILIBRIA

3.1 Introduction

Multiphase and solution thermodynamics deal with the composition of two or more phases in equilibrium. Thus, the maximum concentration of a species in an aqueous stream in contact with an organic stream can be estimated by these calculations. This can establish the contaminant levels obtained in various wastewater streams. A second major application is in partitioning of a pollutant into various phases in the environment. These multiphase thermodynamic calculations are important in design of heterogeneous reactors. In this section, we provide some basic definitions and illustrate the applications of thermodynamic models to waste minimization.

First, we provide various definitions for thermodynamic equilibrium and then illustrate them with applications.

3.2 Vapor-Liquid Equilibrium

The ratio of the composition measure such as (mole fraction) in the vapor phase to that in the liquid phase at equilibrium is referred to as the K-value. Note that $K_y$ is dimensionless.

$$K_{yi} = \left( \frac{y_i}{x_i} \right)_{eq} \quad (1)$$

where $y_i$ is the mole fraction of species $i$ in the vapor phase and $x_i$ is the liquid.

For ideal solutions, the Raoults law applies. This can be stated as follows. At equilibrium the partial pressure of a species in the gas phase, $P_i$, is equal to the mole fraction of the species in the liquid phase, $x_i$, multiplied by its vapor pressure, $P_{vap}$, at the given temperature. It is also equal to the product of the mole fraction in the gas phase, $y_i$, and total pressure, $P$.

$$P_i = x_i P_{vap} = y_i P \quad (2)$$

Hence, Raoults law can also be stated as:

$$y_i = x_i \frac{P_{vap}}{P} \quad (3)$$

Therefore, the K-factor for ideal mixtures is:

$$K_{yi} = \frac{P_{vap}}{P} \quad (4)$$

For non-ideal solutions, the K-factors can be calculated using the activity coefficients. However, for many environmental applications, one can use experimentally reported K-factors. These calculations are, for example, useful to find the composition of the vapor phase in contact with the liquid in the reactor. If there is a fugitive emission, then we can estimate the amount of the toxic chemicals that has inadvertently escaped to the atmosphere. Vapor-liquid equilibrium is also useful in estimating the maximum concentration of VOC in a mixture.

For dilute solutions, or for gaseous species, Henry’s law, given by Eq. (5) is more convenient.

$$x_i = H_i y_i P \quad (5)$$

where $H_i$ is the Henry’s law constant, (atm$^{-1}$) and $P$ (atm) is the total pressure. With this definition, we find that $K_y$-factor is...
Vapor pressure data is often needed to estimate the levels of VOC emissions at various temperatures. The data for pure liquids are well represented by the Antoine equation.

\[
\log_{10}(P^*) = A - \frac{B}{T + C}
\]  

(7a)

or by an empirical extended Antoine equation:

\[
\ln(P_{vap}) = k_1 + \frac{k_2}{k_3 + T} + k_4T + k_5\ln T + k_6T^k
\]  

(7b)

3.3 Gas-Liquid Systems

Phase equilibrium between a dissolving gas, A, and its dissolved concentration, \([A \cdot H_2O]\) or \([A]\), in water is often expressed (for dilute systems) through the equilibrium constant \(K_A\)

\[
K_A = \frac{[A \cdot H_2O]}{P_A} \text{ mol} \cdot L^{-1} \text{ atm}^{-1}
\]  

(8)

which is a function of temperature

\[
\frac{d \ln K_A}{dT} = \frac{\Delta H_{Aeb}}{RT^2}
\]  

(9)

where

\[
\Delta H_{Aeb} = \bar{H}_{A_{sol}} - \bar{H}_{A_{gas}}
\]

is the heat of absorption. Typically \(\Delta H_{Aeb} < 0\) so that as temperature increases the equilibrium constant decreases. Actually, this equilibrium constant is called Henry's constant in environmental chemistry and is independent of composition for dilute solutions.

\[
[A \cdot H_2O] = H_A P_A \quad H_A \left[ \text{M atm}^{-1} \right]
\]  

(10)

Note that the units of \(H_A\) are now (mole/L atm) and M means mole/liter.

Large \(H_A\) implies a very soluble gas. Low \(H_A\) is a slightly soluble gas. (Attention: some books define the reciprocal of \(H_A\) as Henry's constant). The solubility of various gases is indicated in Table 3.1.

A dimensionless Henry's constant, \(\hat{H}_A\), is obtained if gas concentration is used in its definition instead of partial pressure, i.e. \([A]_g = P_A / RT\)

\[
\hat{H}_A = H_A RT = \frac{[A \cdot H_2O]}{[A]_g}
\]  

(11)

Note that depending on the composition measures used to define equilibrium, Henry’s constants appear with different units e.g. \(\bar{H}_A (atm^{-1})\), \(H_A (M \text{ atm}^{-1})\), \(\hat{H}(-)\). It is unfortunate that the chemical engineering and some environmental engineering literature use the reciprocal of the above defined Henry’s constant under the same name! We have adopted here the definitions prevalent in the
environmental chemistry literature although the chemical engineering approach is the older and the better established one. A website posted as part of the course gives the various definitions and conversion factors (http://www.mpch-mainz.mpg.de/~sander/res/henry.html).

The following relationship holds between the above constants

\[
\hat{H}_A = \frac{K_A}{C_{L,TOT}} = \frac{H_A}{C_{L,TOT}} = \frac{\hat{H}_A}{C_{L,TOT} RT}
\]  

(12)

Where \( C_{L,TOT} \) is the total liquid molar concentration.

<table>
<thead>
<tr>
<th>TABLE 3.1: Henry's Law coefficients of atmospheric gases dissolving in liquid water(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas</strong></td>
</tr>
<tr>
<td>O(_2)</td>
</tr>
<tr>
<td>NO</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
</tr>
<tr>
<td>O(_3)</td>
</tr>
<tr>
<td>NO(_2) (^b)</td>
</tr>
<tr>
<td>N(_2)O</td>
</tr>
<tr>
<td>CO(_2) (^c)</td>
</tr>
<tr>
<td>SO(_2) (^c)</td>
</tr>
<tr>
<td>HNO(_2) (^e)</td>
</tr>
<tr>
<td>NH(_3) (^b)</td>
</tr>
<tr>
<td>HCl</td>
</tr>
<tr>
<td>HCHO (^f)</td>
</tr>
<tr>
<td>H(_2)O</td>
</tr>
<tr>
<td>HNO(_3)</td>
</tr>
</tbody>
</table>

\(^a\) Adapted from Schwartz (1983) and Martin (1984c).

\(^b\) Physical solubility only. Dissolved NO\(_2\) reacts with liquid water.

\(^c\) Physical solubility only. These species participate in acid-base equilibria that are not reflected in the values of \( H \) given.

\(^d\) Ozone is actually a reacting solute in water (Roth and Sullivan, 1981).

For our purposes here we will use only the Henry's law coefficient as presented here and as a function of temperature in Table 3.4. The Henry's law coefficient of Roth and Sullivan is presented as \( H = 3.84 \times 10^7 \text{ (OH}^-\) exp\((2428/T) \text{ [atm mole fraction]}^{-1}\) defined by \( p_x = H_{x} x_{x}\).

\(^e\) A more recent measurement of the H\(_2\)O Henry's law constant is that of Yoshizumi et al. (1984) who report \( H_{H_{2}O} = 1.42 \times 10^{16} \text{ M atm}^{-1}\) at 293 K.

\(^f\) HCHO exists in solution primarily in the gem-diol form: HCHO + H\(_2\)O = H\(_2\)C(OH)\(_2\). The Henry's law coefficient given in the table includes both dissolved HCHO and H\(_2\)C(OH)\(_2\).

3.3.1 Water Ionization

The ionization or recombination reaction for water is for all practical purposes infinitely fast

\[
H_2O \leftrightarrow H^+ + OH^-
\]  

(13)

so that equilibrium is always established

\[
K_w' = \left[H^+\right]\left[OH^-\right]/\left[H_2O\right] = 1.82 \times 10^{-16} \text{ M at 298 K}
\]  

(14)

Since molar concentration of water is constant, we get

\[
K_w = \left[H^+\right]\left[OH^-\right] = 1.0 \times 10^{-14} \text{ M}^2 \text{ at 298 K}
\]  

(15)
For pure water $[H^+] = [OH^-] = 1.0 \cdot 10^{-7}$ M. Recall that

$$pH = -\log [H^+]$$

so that $pH = 7$ for pure water at 298K.

### 3.3.2 Carbon Dioxide/Water Equilibria

Carbon dioxide is prevalent in the atmosphere and undergoes the following equilibriations in water (with equilibrium constant for each step indicated in parentheses)

$$CO_2(g) + H_2O \rightleftharpoons CO_2\cdot H_2O \quad (K_{ch})$$

$$CO_2\cdot H_2O \rightleftharpoons H^+ + HCO_3^- \quad (K_{c1})$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad (K_{c2})$$

We can express now the concentration of dissolved carbon containing species (ions) in terms of these constants

$$[CO_2\cdot H_2O] = K_{ch} p_{co2} = H_{co2} p_{co2}$$

$$[HCO_3^-] = \frac{K_{c1}[CO_2\cdot H_2O]}{[H^+]^2} = \frac{H_{co2} K_{c1} p_{co2}}{[H^+]^2}$$

$$[CO_3^{2-}] = \frac{K_{c2}[HCO_3^-]}{[H^+]} = \frac{H_{co2} K_{c1} K_{c2} p_{co2}}{[H^+]^2}$$

We also must always satisfy the electroneutrality relation

$$[H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

Upon substitution of the above expressions into the electroneutrality equation we get:

$$[H^+] = \frac{H_{co2} K_{c1} p_{co2}}{[H^+]} + \frac{2H_{co2} K_{c1} K_{c2} p_{co2}}{[H^+]} + \frac{K_w}{[H^+]}$$

Upon rearrangement a cubic equation for $[H^+]$ results

$$[H^+]^3 - [K_w + H_{co2} K_{c1} p_{co2}][H^+] - 2H_{co2} K_{c1} K_{c2} p_{co2} = 0$$

Given the temperature, $T$, and partial pressure of $CO_2$, $p_{co2}$, the hydrogen ion concentration $[H^+]$ can be calculated from the above equation and pH obtained. (For temperature dependence see Table 3.2).

At $p_{co2} = 330$ ppm ($= 3.3 \times 10^{-4}$ atm) at 283°K the solution pH = 5.6 ([$H^+$] = 2.51 x $10^{-6}$ (mol/L)). This is often called the pH of "pure" rain water.
TABLE 3.2: Thermodynamic data for calculating temperature dependence of aqueous equilibrium constants

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>ΔH_{298}, kcal mole^{-1}</th>
<th>K at 298 K, M</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2O ↔ H^+ + OH^-</td>
<td>13.345</td>
<td>1.008 \times 10^{-14}</td>
</tr>
<tr>
<td>CO_3^2- · H_2O ↔ H^+ + HCO_3^-</td>
<td>1.825</td>
<td>4.283 \times 10^{-7}</td>
</tr>
<tr>
<td>HCO_3^- ↔ H^+ + CO_3^2^-</td>
<td>3.55</td>
<td>4.687 \times 10^{-11}</td>
</tr>
<tr>
<td>NH_3 · H_2O ↔ NH_4^+ + OH^-</td>
<td>8.65</td>
<td>1.709 \times 10^{-5}</td>
</tr>
<tr>
<td>SO_3^- · H_2O ↔ H^+ + HSO_3^-</td>
<td>-4.161</td>
<td>1.29 \times 10^{-3}</td>
</tr>
<tr>
<td>HSO_3^- ↔ H^+ + SO_3^{2-}</td>
<td>-2.23</td>
<td>6.014 \times 10^{-4}</td>
</tr>
</tbody>
</table>

*Maahas (1982) has reviewed the data on SO_3/H_2O equilibria and has recommended the following values of K_{s1}, K_{s2}, and K_{s3}:

\[
\log K_{s1} = \frac{1376.1}{T} - 4.521
\]
\[
\log K_{s2} = \frac{853}{T} - 4.74
\]
\[
\log K_{s3} = \frac{621.9}{T} - 9.278
\]

3.3.3 Sulfur Dioxide/Water Equilibrium

The scenario is similar as in the case of CO_2 absorption

\[
SO_2(g) + H_2O \rightarrow SO_2 \cdot H_2O \quad H_{SO_2}
\] (21a)

\[
SO_2 \cdot H_2O \rightarrow H^+ + HSO_3^- \quad K_{s1}
\] (21b)

\[
HSO_3^- \rightarrow H^+ + SO_3^{2-} \quad K_{s2}
\] (21c)

The concentrations of dissolved species are

\[
[SO_2 \cdot H_2O] = H_{SO_2} \cdot P_{SO_2}
\] (22a)

\[
[HSO_3^-] = \frac{H_{SO_2} \cdot K_{s1} \cdot P_{SO_2}}{[H^+]}
\] (22b)

\[
[SO_3^{2-}] = \frac{H_{SO_2} \cdot K_{s1} \cdot K_{s2} \cdot P_{SO_2}}{[H^+]^2}
\] (22c)

Satisfying the electroneutrality relation requires

\[
[H^+]^3 - \left(K_w + H_{SO_2} \cdot K_{s1} \cdot P_{SO_2}\right)[H^+] - 2H_{SO_2} \cdot K_{s1} \cdot K_{s2} \cdot P_{SO_2} = 0
\] (23)

The total dissolved sulfur in oxidation state + 4 is S(IV) and its concentration is given by

\[
[S(IV)] = H_{SO_2} \cdot P_{SO_2} \left[1 + \frac{K_{s1}}{[H^+]} + \frac{K_{s1} \cdot K_{s2}}{[H^+]^2}\right] = H_{S(IV)}^* \cdot P_{SO_2}
\] (24)

where \(H_{S(IV)}^*\) is the modified Henry's constant which we can express as

\[
H_{S(IV)}^* = H_{SO_2} \left[1 + 10^{pH} \cdot K_{s1} + 10^{2\cdot pH} \cdot K_{s1} \cdot K_{s2}\right]
\] (25)
Clearly the modified constant $H^*$ is dependent on pH. The larger the pH, i.e. the more alkaline the solution, the larger the equilibrium content of $S\ (IV)$. This is illustrated in Figure 3.2 for $p_{SO_2} = 0.2$ ppb and 200 ppb.

**FIGURE 3.2: Equilibrium dissolved S(IV) as a function of pH, gas-phase partial pressure of SO$_2$ and temperature**

<table>
<thead>
<tr>
<th>$[S(IV)]$, M</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-6}$</td>
<td>0</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>1</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>2</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>3</td>
</tr>
<tr>
<td>$10^{-2}$</td>
<td>4</td>
</tr>
<tr>
<td>$10^{-1}$</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>6</td>
</tr>
</tbody>
</table>

Let us express now mole fractions of various dissolved sulfur species as function of pH (really these are mole ratios, i.e. moles of a particular sulfur species divided by total moles of $S\ (IV)$ or mole fractions on water free basis since water is the dominant component.

\[
\begin{align*}
\alpha_0 &= X_{SO_2\cdot H_2O} = \frac{[SO_2\cdot H_2O]}{[S\ (IV)]} = \left[1 + K_{s1} 10^{-pH} + K_{s1} K_{s2} 10^{-2pH}\right]^{-1} \\
\alpha_1 &= X_{HSO_3^-} = \frac{[HSO_3^-]}{[S\ (IV)]} = \left[1 + K_{s1} 10^{-pH} + K_{s2} 10^{-pH}\right]^{-1} \\
\alpha_2 &= X_{SO_3^-} = \frac{[SO_3^-]}{[S\ (IV)]} = \left[1 + K_{s2} 10^{-pH} + (K_{s1} K_{s2})^{-1} 10^{-2pH}\right]^{-1}
\end{align*}
\]

(26a)  
(26b)  
(26c)

Common notation for these are $\alpha_0, \alpha_1, \alpha_2$ in aquatic chemistry.

Figure 3.3 illustrates the above three mole fractions for $p_{SO_2} = 10^{-9}$ atm (1 ppb). Since these species have different reactivities pH will affect reaction rates. At low pH $SO_2\cdot H_2O$ dominates, at high pH all $S\ (IV)$ is in the form of $SO_3^-$. Intermediate pH contains mainly $HSO_3^-$. 

6
FIGURE 3.3: Mole fractions and concentrations of the three dissolved S(IV) species, $SO_2 \cdot H_2O$, $HSO_3^-$, and $SO_4^{2-}$, as a function of pH at $T = 298 K$, and $p_{SO_2} = 10^{-9} \text{ atm (1ppb)}$.

3.3.4 Abundance of Liquid Water in the Atmosphere

Liquid water content is expressed in (g water/m$^3$ air) or (m$^3$ water/m$^3$ air). Let $L$ be the second dimensionless measure. Then

- clouds: $L = 10^{-7}$ to $10^{-6}$
- fog: $L = 10^{-8}$ to $5 \times 10^{-7}$
- aerosols: $L = 10^{-11}$ to $10^{-10}$

The distribution of a species A between gas and aqueous phases, in say a cloud, can be expressed as

$$\frac{\text{moles of } A \text{ in solution per } m^3 \text{ of air}}{\text{moles of } A \text{ in air per } m^3 \text{ of air}} = \frac{H_A P_A L}{RT} = H_A RTL \quad (27)$$

- $H_A RTL << 1$ species A is mainly in the gas
- $H_A RTL >> 1$ species A mainly in the liquid

For $L = 10^{-6}$, $(RTL)^{-1} \approx 4 \times 10^4 \text{ M atm}^{-1}$

Hence for

- $H_A << 4 \times 10^4 \text{ M atm}^{-1}$ species A in the gas
- $H_A >> 4 \times 10^4 \text{ M atm}^{-1}$ species A in the liquid
Table 3.1 indicates that, with exception of \( HC \ell \), \( HCHO \) and especially \( H_2O_2 \) and \( HNO_3 \), other species will remain mainly confined to the gas phase.

For \( SO_2 \) at \( pH = 4 \), \( H^{*}_{S(IV)} \approx 10^2 \) and at \( L = 10^{-6} \) \( H^{*}_{S(IV)} \leq (RTL)^{-1} \) and most of (almost all of) the \( S(IV) \) is in the gas phase. In contrast for \( HNO_3 \) the modified Henry’s constant is

\[
H^* = 10^{10}
\]

and all of nitric acid is in solution.

### Maximum Solubility

For example, the equilibrium dissolved concentration of \( A \) is given by \([A_g] = H_A P_A \) but the total amount of species present in a closed system (i.e. system with fixed boundaries over which no exchange of matter occurs with the surroundings) is:

\[
N_{tot_A} = C_{A_g} V_g + C_{A_l} V_L
\]

\[
= V_g \left[ C_{A_g} + C_{A_l} \frac{V_L}{V_g} \right] = V_g \left[ \frac{P_A}{RT} + C_{A_l} L \right]
\]

(28)

Dividing by air volume, \( V_g \), we get:

\[
\frac{N_{tot_A}}{V_g} = C_{A_{tot}} = \frac{P_{A_{tot}}}{RT} = \frac{P_A}{RT} + C_{A_l} L
\]

(29)

Since the following relationship holds

\[
C_{A_l} = H_A P_A
\]

(30)

Substituting eq(30) into eq(29) yields

\[
\frac{P_{A_{tot}}}{RT} = P_A \left[ \frac{1}{RT} + H_A L \right] = \frac{P_A}{RT} \left[ 1 + H_A RTL \right]
\]

(31)

Solving for the partial pressure of \( A \) gives:

\[
P_A = \frac{P_A}{1 + H_A RTL}
\]

(32)

Using eq (30) we get the concentration of dissolved \( A \) in water:

\[
C_{A_l} = \frac{H_A P_A}{1 + H_A RTL}
\]

Then, when gas solubility is very high so that \( H_A RTL \gg 1 \) the maximum concentration of dissolved \( A \) is:

\[
C_{A_{max}} = \frac{P_A}{RT L} = [A]_{max}
\]

(33)

Thus, essentially all of the soluble gas is in the liquid phase!
Clearly, then, in a closed system for a very highly soluble gas we must take precautions in calculating the equilibrium composition not to violate the mass balance, (i.e. "not to dissolve more gas than there is available") as the concentration of eq (33) cannot be exceeded. Say $P_A = 10^{-9}$ atm (1 ppb) and $L = 10^{-6}$, $[A]_{\text{max}} = 4 \times 10^{-5}$ M. Regardless of the value of $H$, say $H = 10^{10}$ and $[A]_{\text{eq}} = 10$ M, clearly $[A]_{\text{max}}$ cannot be exceeded. $[A]_{\text{max}}$ can only be exceeded if the water droplets are brought into contact with much larger volume of air not just the volume containing $L$ amount of water.

### 3.4 Liquid-Liquid Systems

For immiscible liquid-liquid systems, the K-factors are known more commonly as the distribution coefficients.

$$K_{D,j} = \frac{x_i^{(1)}}{x_i^{(2)}}$$

(34)

where (1) and (2) refer to liquid phases 1 and 2 with $x_i$ as the mole fraction of species $i$ in the corresponding phase. For gas-solid or liquid-solid systems the equilibrium is described by adsorption equilibrium constants which will be addressed in a subsequent chapter.

Liquid-liquid equilibria can also be expressed in terms of a ratio of concentrations $K = C_o/C_w$ where $C_o$ is the concentration in the organic phase and $C_w$ is the concentration in the water phase.

One important parameter widely used is environmental engineering is the octanol-water partition coefficient usually denoted $K_{ow}$. This is defined as the ratio of concentration of the solute in n-octanol to that in water. The essential idea behind the use of this parameter is that n-octanol can be viewed as representative to the lipid phase in tissues and, hence, this quantity is a measure of how the solute gets incorporated into the tissues. Hence accurate estimates or experimental values of this parameter is of importance in estimating the bio-toxicity of a compound. A related parameter is the bio-concentration factor $BCF$ which is defined as follows:

$$\log BCF = 0.79 \log (K_{ow}) - 0.40$$

(35)

Thus, $BCF$ is proportional to $K_{ow}$. If $BCF$ is greater than 1000 then the compound is considered to have a high potential for bioaccumulation. If $BCF$ is less than 250 then the compound is assumed to have low potential to accumulate in aquatic species.

Predictive methods based on group contributions are available for $K_{ow}$ and these are useful as a first estimate for a new compound in the absence of measured values.

Example: Phenol has a $\log (K_{ow})$ value of 1.46. What is its bio-concentration potential?

Answer: Using the equation above we find $\log (BCF) = 0.7771$

$BCF = 10^{0.7771}$ which is less than 250.

Hence phenol has low bio-accumulation potential.

### 3.5 Multiphase Distribution

Situations where multiphase equilibria, when more than two phases co-exists, need to be assessed are optly illustrated by Figure 3.5 taken from Seader and Henley (1998) where 7 phases are reported.
Air
\(n\)-hexane-rich liquid
Aniline-rich liquid
Water-rich liquid
Phosphorous liquid
Gallium liquid
Mercury liquid

**Figure 3.5 Seven Phases in Equilibrium**

In some applications of multiphase systems, three or more phases coexists. Figure 3.5 is a schematic diagram of an experiment taken from Hildebrand (1970), which shows seven phases in equilibrium at near-ambient temperature. The phase on top is air, followed by six liquid phases in order of increasing density: hexane-rich, aniline-rich, water-rich, phosphorous, gallium and mercury. Each phase contains all components in the seven-phase mixture, but the mole fractions in many cases are extremely small. For example, the aniline-rich phase contains on the order of 10 mol % \(n\)-hexane, 20 mol % water, but much less than 1 mol % each of dissolved air, phosphorous, gallium and mercury. Note that even though the hexane-rich phase is not in direct contact with the water-rich phase, an equilibrium amount of water (approximately 0.06 mol %) is present in the hexane-rich phase. This is so because each phase is in equilibrium with each of the other phases as attested by the equality of component fugacities:

\[
\left( f_{1}^{(1)} = f_{1}^{(2)} = f_{1}^{(3)} = f_{1}^{(4)} = f_{1}^{(5)} = f_{1}^{(6)} = f_{1}^{(7)} \right)_{\text{eq}}
\]

(This is true for all \(i\) (i.e. all components in the system)).

Note that the fugacity of a component must be the same in all phases if the phases are to be in equilibrium. In \(f_{i}^{(j)}\) the superscript \(j\) denotes the phase and subscript \(I\) the chemical component.

### 3.6 Partitioning of Pollutants: Level I Model

The environment is divided into four compartments: air, water, soil and biota. Each component is assigned a certain volume denoted by \(V_i\). The concentration distribution of a pollutant discharged into any of the phases (say air), can be calculated by using the concept of fugacity. The fugacity of a component (designated as \(f\) here) is the same in all the compartments at equilibrium. For calculation purposes, a concept called “fugacity capacity” is more useful. This is defined by the following equation.

\[
c_i = z_i f
\]

where \(c_i =\) pollutant concentration in compartment \(i\)  
and \(z_i =\) fugacity capacity for the compartment \(i\)

Now consider an amount of pollutant \(M_T\) released to the environment. \(M_T\) has units of mass. The release may be to one or more of the compartments. Then by mass balance at equilibrium for a closed system

\[
M_T = \sum c_i V_i
\]

Using the definition of fugacity capacity, we have

\[
M_T = f \sum z_i V_i
\]
Hence \( f = \frac{M_T}{\sum z_i V_i} \) \hspace{1cm} (39)

Pollutant concentration in compartment \( i \) at equilibrium is equal to
\[
c_i = M_T \frac{z_i}{\sum z_i V_i}
\] \hspace{1cm} (40)

Pollutant total mass in any compartment \( i \) \( M_i = c_i V_i \) is
\[
M_i = M_T \frac{z_i V_i}{\sum z_i V_i}
\] \hspace{1cm} (41)

Percentage distribution to compartment \( i \) is then directly calculated as
\[
\frac{M_i}{M_T} \times 100 = \left( \frac{z_i V_i}{\sum z_i V_i} \right) \times 100
\] \hspace{1cm} (42)

Note that the fugacity need not be explicitly calculated when using this approach. One needs the information only on the fugacity capacity. We now show how these can be obtained from basic thermodynamic properties. Also note that the above procedure can be repeated for a number of pollutants.

3.6.1 Fugacity capacity in air phase
Fugacity of a component at ideal state in the air phase is equal to its partial pressure \( p \), and the concentration is equal to \( p/RT \). Hence, using the definition of fugacity capacity
\[
z_{air} = \frac{1}{RT}
\] \hspace{1cm} (43)

which has a value of \( 4.04 \times 10^{-4} \) mol / m\(^3\).Pa at 25\(^\circ\)C. The fugacity capacity in air is independent of the chemical species and has a constant value at a fixed temperature.

3.6.2 Water phase
In aqueous systems, the fugacity of a chemical is
\[
f = x\gamma P_{vap}
\] \hspace{1cm} (44)

where \( x \) is the mole fraction and \( \gamma \) is the activity coefficient. If the solute is in equilibrium with the gas then \( f = p \). By Henry’s law \( c_i = H_p \).

Hence, we have
\[
z_{water} = H
\] \hspace{1cm} (45)

where \( H \) is the Henry’s law constant in \( (mol/m^3 pa) \).

3.6.3 Soil phase
Chemicals in soil are almost always adsorbed into the natural organic matter and are in equilibrium with the water phase concentration. Concentration in soil is related to concentration in water by the adsorption equilibrium constant.
\[ c_{\text{soil}} = K_{\text{soil}} c_{\text{water}} \quad (46) \]

A measure of \( K_{\text{soil}} \) is \( K_{\text{oc}} \), the organic carbon based distribution coefficient. \( K_{\text{oc}} \) represents the concentration per unit mass of organic carbon in soil. If \( \phi_{\text{soil}} \) represents the mass fraction of carbon in the soil, then a measure of \( K_{\text{soil}} \) is the product \( K_{\text{oc}} \phi_{\text{oc}} \) where \( \phi_{\text{oc}} \) is the mass fraction of carbon. Hence the fugacity capacity of soil is
\[ z_{\text{soil}} = HK_{\text{oc}} \phi_{\text{soil}} \rho_{\text{soil}} \quad (47) \]

Further \( K_{\text{oc}} \) is shown to correlate well with octanol-water partition coefficient \( K_{\text{ow}} \) with the equality \( K_{\text{oc}} = 0.41 K_{\text{ow}} \). With these, we find
\[ z_{\text{soil}} = 0.41 H K_{\text{ow}} \phi_{\text{soil}} \rho_{\text{soil}} \quad (48) \]

For biota equation (49) below is used
\[ z_{\text{biota}} = 0.05 K_{\text{ow}} H \rho_{\text{biota}} \quad (49) \]

where \( \phi_{\text{biota}} \) is the mass fraction of organic carbon in the biota phase.

**Example:**
Consider 100 mol of PCP (pentachlorophenol) released into the aqueous phase. Find its distribution in various compartments using the equilibrium (fugacity level 1) model.

**Solution:**
We need some data for the volumes of various compartments and some thermodynamic properties of PCP.

Assume these volumes. These are typical values used in these calculations
\[
V_{\text{air}} = 10^{14} \text{ m}^3; \quad \text{water} = 2 \times 10^{11} \text{ m}^3
\]
\[
\text{soil} = 9 \times 10^9 \text{ m}^3, \quad \text{biota} = 2 \times 10^5 \text{ m}^3
\]

**Thermodynamic data.**

Reciprocal of the Henry’s law constant \( H^{-1} = 0.079 \text{ Pa m}^3/\text{mole} \) (from the literature).
Also \( K_{\text{ow}} = 112,202 \)

Now we can calculate the fugacity capacity values for the four phases.
\[
z_{\text{air}} = \frac{1}{RT} = 4.04 \times 10^{-4} \frac{\text{mol}}{\text{m}^3 \text{ Pa}} \text{ at } 25^\circ \text{C}
\]
\[
z_{\text{water}} = H = 12.66 \frac{\text{mol}}{\text{m}^3 \text{ Pa}}
\]
\[
z_{\text{soil}} = 0.41 H K_{\text{ow}} \phi_{\text{soil}} \rho_{\text{soil}}.
\]

\( \phi_{\text{soil}} \) = the mole fraction of organic carbon. We use a value of 0.02 here.
\( \rho_{\text{soil}} = 2400 \text{ kg/m}^3 \).
Using these values
\[ z_{soil} = 2.8 \times 10^4 \text{ mol/m}^3 \text{ Pa}. \]

Similarly we use \( \rho_{biota} = 1000 \text{ kg/m}^3 \) and find
\[ z_{biota} = 7.1 \times 10^4 \text{ mol/m}^3 \text{ Pa}. \]

With all this information we can find the equilibrium of the pollutant distribution. The calculations can be done conveniently in an excel spreadsheet or using the matlab program shown here.
\[ \sum z_i v_i = 2.55 \times 10^4 \text{ mol/m}^3 \]

Percentage partition is then calculated as \( z_i v_i / \sum z_i v_i \) and the results are
\( \text{air} = 1.59 \times 10^{-2} \% \quad \text{water} = 0.995 \% \quad \text{soil} = 99.4 \% \quad \text{Fish (biota)} = 5.58 \times 10^{-3} \% \).

PCP tends to accumulate in soil.

---

% MATLAB PROGRAM FOR FUGACITY LEVEL 1 CALCULATIONS.
% 1= air, 2 = water, 3 = soil ; 4 = biota.
% PCP data used here
henry = 0.079 ;  % Pa-m^3.mole
kow = 112202 ;  % L/kg
phi_soil = 0.02 ;  % organic mass fraction in soil
temp = 298.0 ;
% calculation section
volume = [ 1e+14
    2e+11
    9e+09
    2e+05];
rho_soil = 2400.0;
rho_biotas = 1000.0 ;
z(1) = 1.8314 /temp;
z(2) = henry ;
z(3) = 0.41*phi_soil*rho_soil*kow/henry/1000.;
z(4) = 0.05*rho_biotas*kow/henry/1000.0 ;
sum = z * volume 
distribution(1) = z(1) * volume(1) / sum;
distribution(2) = z(2) * volume(2) / sum;
distribution(3) = z(3) * volume(3) / sum;
distribution(4) = z(4) * volume(4) / sum;
distribution

References:


Converting Henry Law Constant

http://www.mpch-mainz.mpg.de/~sander/res/henry-conv.html
Introduction to Chemical Reaction Engineering and Some Definitions (CHE 471)
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ChE 471 – LECTURE 1

1 Introduction to Chemical Reaction Engineering and Some Definitions

Whenever there is a change in the atomic content, or atomic configuration, of a molecule of a particular chemical species brought about by interaction with molecules of other chemical species, or due to an input of energy, a chemical reaction takes place! Such chemical transformations form the basis for manufacture of new chemicals, pharmaceuticals, fuels and materials and also occur in nature. Being able to conduct chemical reactions at controlled conditions with maximum selectivity, yield and energy efficiency, while minimizing the consequences to the environment, is one of the key tasks of chemical reaction engineering. The other is the development of quantitative understanding of the reactions in the natural environment and their interactions with the chemical species generated and/or released by man, and design of methods for pollution prevention and abatement. Finally, selecting appropriate reactions and executing them in a controlled fashion in production of specialty materials, pharmaceuticals, feed, food and a variety of consumer products is yet another task of chemical reaction engineering (CRE).

Chemical reaction engineering (CRE) is thought of as a blend of applied chemical kinetics and chemical thermodynamics by industrial chemists, who view it as a set of procedures by which one can determine how far a certain reaction can proceed (chemical equilibrium) and at what rate, depending on process conditions, can that final state be approached. Chemical engineers think of CRE as the subject of chemical reactor design, which, ideally, for important large-scale processes, requires them to master and follow the procedure specified below in steps a) through j).

a) Establish reaction mechanism
b) Collect rate data free of transport limitations.
c) Correlate rate data by mathematical equation or otherwise.
d) Formulate suitable models for reactor design and select reactor type (i.e. ideal flow pattern).
e) Account for nonideality of real reactors and for the effect of physical transport processes.
f) Select reactor size and operating conditions.
g) Specify key reactor elements.
h) Specify auxiliary equipment.
i) Specify methods of control.
j) Specify start-up and shut-down procedures.

Schematically, the body of knowledge and activities involved in reactor design are summarized in Figure 1.
We will now consider in turn some of the basic definitions needed for appropriate chemical reaction engineering analysis.
1.1 Reaction Stoichiometry

Chemical reaction engineering analysis is much facilitated if reaction stoichiometry is well known. Reaction stoichiometry represents the application of the principle of conservation of mass to a particular reaction under consideration.

Single Reaction stoichiometry can always be written as:

$$\sum_{j=1}^{s} \nu_j A_j = 0$$

where the following designations and definitions are used:
- $A_j$ – chemical species $j$
- $\nu_j$ - stoichiometric coefficient of $j$
- $s$ – total number of species

By Convention
- $\nu_j > 0$ for products
- $\nu_j < 0$ for reactants

Equation (1), due to mass conservation, implies

$$\sum_{j=1}^{s} \nu_j M_j = 0$$  \hspace{1cm} (1-1a)

where $M_j$ = molecular weight of species $j$.

For example, for sulfur dioxide oxidation, the stoichiometry and species designation can be written as:

$$SO_2 + \frac{1}{2} O_2 = SO_3$$

e.g. $A_1 = SO_2$, $A_2 = O_2$, $A_3 = SO_3$

$$\nu_1 = -1, \nu_2 = -\frac{1}{2}, \nu_3 = 1$$

1.2 Progress of Reaction

1.2.1 Molar Extent

To monitor reaction progress we introduce the concept of (molar) extent of reaction, which for a batch system (no inlets and outlets) is defined by equation (1-2).

$$\frac{n_j - n_{j,0}}{\nu_j} = X$$  \hspace{1cm} Batch System  \hspace{1cm} (1-2)
\[
n_j = n_{jo} + \nu_j X
\]  \hspace{1cm} (1-2a)

where

- \(n_j\) – number of moles of species j, (mol)
- \(n_{jo}\) – initial number of moles of j, (mol)
- \(X\) – (molar) extent of reaction or degree of advancement (mol)

In a flow system at steady state

\[
\frac{F_j - F_{j,o}}{\nu_j} = \dot{X}
\]

Flow System  \hspace{1cm} (1-3)

\[
F_j = F_{j,o} + \nu_j \dot{X}
\]

Steady state  \hspace{1cm} (1-3a)

- \(F_j\) – molar flow rate of species j, (mol s\(^{-1}\))
- \(F_{j,o}\) – molar flow rate of j in the feed, (mol s\(^{-1}\))
- \(\dot{X}\) – extent of reaction, (mol s\(^{-1}\))

Reaction extent is an extensive measure of reaction progress (e.g. moles or moles/s). Often it is normalized based on mass or mass flow rate of the system, or made unitless by dividing it with total moles in the feed or total moles at conditions of interest. Clearly one should be careful as to how reaction extent is defined.

1.2.2 Fractional Conversion

In order to define another unitless measure of reaction progress it is necessary to introduce the concept of the limiting reactant first.

**Limiting reactant** is the reactant present in amount less than or equal to the amount required by stoichiometry for reaction completion.

\[
X_{\text{max}} = \min_j \left\{ \frac{n_{jo}}{\nu_j} \right\}
\]  \hspace{1cm} (1-4a)

or

\[
\dot{X}_{\text{max}} = \min_j \left\{ \frac{F_{j,o}}{(\nu_j)} \right\}
\]  \hspace{1cm} (1-4b)

Equation (1-4a) or (1-4b) identifies the limiting reactant, call it A, i.e. the reactant with the smallest ratio of the moles in the feed and the absolute value of its stoichiometric coefficient.
Alternative notation for reaction stoichiometry is often used as:

\[ aA = bB = pP \text{ (s)} \]

with \(a, b, p\) all positive. Clearly, \(v_A = -a, v_B = -b, v_p = P\) establishes the link between eq (1-5) and eq (1-1).

Fractional conversion of limiting reactant A (e.g., \(j = A\)) is defined by

\[ x_A = \frac{(\text{moles reacted})}{(\text{moles fed})} = \frac{n_{A_0} - n_A}{n_{A_0}} \quad \text{Batch} \]  

\[ x_A = \frac{F_{A_0} - F_A}{F_{A_0}} \quad \text{Flow} \]

The relations to molar extent are self evident.

Number of moles reacted:

\[ n_{A_0} x_A = (-v_A)X \quad (7a) \]

Molar flow rate reacted:

\[ F_{A_0} x_A = (-v_A)\dot{X} \quad (7b) \]

The relationship between molar quantities of any species, \(j\), and those for the limiting reactant, A, using fractional conversion are:

\[ n_j = n_{j,0} + \frac{v_j}{v_A} \left( n_A - n_{A,0} \right) \quad (1-8a) \]

\[ F_j = F_{j,0} + \frac{v_j}{v_A} \left( F_A - F_{A,0} \right) \quad (1-8b) \]

This can be rewritten as:

\[ n_j = n_{A,0} \left[ M_{j/A} + \frac{v_j}{(-v_A)} x_A \right] \quad (1-9a) \]

\[ F_j = F_{A,0} \left[ M_{j/A} + \frac{v_j}{v_A} x_A \right] \quad (1-9b) \]

where \(M_{j/A} = C_{j_0}/C_{A_0}\)  

1.3 Relationships between Reaction Progress and Measures of Composition

Neither molar extent nor fractional conversion are accessible by direct measurement. However, measures of the composition of the mixture e.g. mole fraction, molar concentration, etc., are readily accessible in direct measurement. It is then necessary to relate the changes in composition to measures of reaction progress as done below.
Molar Concentration of species j is the number of moles of j per unit volume of the system

\[ C_j = \frac{n_j}{V} \quad (1-11a) \quad \text{or} \quad C_j = \frac{F_j}{Q} \quad (1-11b) \]

where

- \( C_j \) – molar concentration of j, (mol/ m³)
- \( V \) – volume of the batch system, (m³)
- \( Q \) – volumetric flow rate in the steady flow system, (m³s⁻¹). Often volumetric flow rate is designated by \( \dot{V} \) or \( Q \).

Total molar concentration then is:

\[ C_{\text{tot}} = \frac{n_{\text{tot}}}{V} = \frac{N}{V} \quad (1-12a) \quad \text{or} \quad C_{\text{tot}} = \frac{F_{\text{tot}}}{Q} \quad (1-12b) \]

where

- \( C_{\text{tot}} \) – total molar concentration of all species (mol m⁻³)

The total number of moles (or total molar flow rate) can then be expressed in terms of reaction extent.

\[ N = n_{\text{tot}} = \sum_{j=1}^{s} n_j = n_{\text{tot},o} + \sum_{j=1}^{s} \nu_j X \quad (1-13a) \]

\[ F_{\text{tot}} = \sum_{j=1}^{s} F_j = F_{\text{tot},o} + \sum_{j=1}^{s} \nu_j \dot{X} = F_{\text{tot},o} + \sum_{j=1}^{s} \nu_j \frac{\dot{X}}{F_{\text{tot},o}} + 1 + \frac{\sum_{j=1}^{s} \nu_j \dot{X}}{F_{\text{tot},o}} \quad (1-13b) \]

The coefficient of expansion \( \varepsilon_A \) is defined by

\[ \varepsilon_A = \frac{\text{(volume of the system at complete conversion of limiting reactant)} - \text{(Initial volume of the system)}}{\text{(Initial volume of the system)}} = \frac{V_{/x_i=1} - V_{/x_i=0}}{V_{/x_i=0}} \quad (1-14) \]

Thus we need an appropriate equation of state to relate the volume of the system, its temperature and pressure and total moles at complete conversion. At constant temperature, constant pressure conditions, the assumption that volume changes in liquids or solids caused by reaction are minimal is justified so that \( V_{/x_i=1} = V_{/x_i=0} \) and \( \varepsilon_A = 0 \). For gases, if we can use the ideal gas equation of state, then:

\[ PV = n_{\text{tot}} RT \quad (1-15) \]
At P, T constant it is clear that the volume, V, is directly proportional to the total number of moles in the system, $n_{tot}$. Therefore, equation (14) with the help of equation (13a) yields:

$$
\varepsilon_A = \frac{n_{tot/x_A = 1} - n_{tot/x_A = 0}}{n_{tot,0}} = \frac{X_{max} \sum_{j=1}^{s} \nu_j}{n_{tot,0}} = y_{Ao} \frac{\sum_{j=1}^{s} \nu_j}{(-\nu_A)}
$$

(1-16)

where $y_{Ao}$ = mole fraction of limiting reactant in the feed.

The following relationship follows:

$$
n_{tot} = n_{tot,0} \left( 1 + \varepsilon_A \frac{X}{X_{max}} \right) = n_{tot,0} \left( 1 + \varepsilon_A x_A \right)
$$

(1-17a)

$$
F_{tot} = F_{tot,0} \left( 1 + \varepsilon_A \frac{\dot{X}}{X_{max}} \right) = F_{tot,0} \left( 1 + \varepsilon_A x_A \right)
$$

(1-17b)

Returning now to the definition of the molar concentration of species j by equation (1-11), we obtain the relation between molar concentration and reaction progress as shown below.

For liquids, assuming negligible change in volume due to reaction, and also for gas phase reactions conducted in a closed batch autoclave, equation (1-11a) yields a linear relation between molar concentration and reaction extent per unit volume or molar concentration and conversion.

$$
C_j = C_{jo} + \nu_j \xi \quad (1-18) \quad \text{with} \quad \xi = \frac{X}{V} \quad \text{or} \quad \xi = \frac{\dot{X}}{Q} \quad (1-19)
$$

$$
C_j = C_{jo} + \frac{\nu_j}{(-\nu_A)} C_{Ao} x_A
$$

(1-20)

For gases, assuming ideal gas mixture in a non-constant volume autoclave

$$
C_j = \frac{T_o P}{TP_o} \left( C_{jo} + \frac{\nu_j X}{V_o} \right) \left[ \frac{\sum_{j=1}^{s} \nu_j}{1 + \frac{\sum_{j=1}^{s} \nu_j}{N_o} X} \right]
$$

(1-21)

or
\[ C_j = C_{oP} \frac{T_oP}{TP_o} \left( \frac{M_{j/A} + \frac{\nu_j}{(-\nu_A)} x_A}{1 + \varepsilon_A x_A} \right) \]  \hspace{1cm} (1-21b)

Recall that the coefficient of expansion, \( \varepsilon_A \) is defined by equation (1-16) while

- \( y_{Ao} \) – mole fraction of A in initial mixture
- \( T_o, P_o \) – initial temperature and pressure
- \( T, P \) – temperature and pressure at the time (place) when (where) concentration is determined
- \( N_o \) – initial total number of moles
- \( F_{tot,o} \) – total molar flow rate of the feed

\[ M_{j/A} = \frac{n_{j,o}}{n_{Ao}} = \frac{C_{j,o}}{C_{Ao}} \] – feed molar ratio of species j to limiting reactant A

In a flow system

\[ C_j = C_{tot,o} \frac{T_oP}{TP_o} \left( \frac{F_{j,o} + \nu_j \bar{X}}{F_{tot,o} + \sum_{j=1}^{n} \nu_j \bar{X}} \right) \]  \hspace{1cm} (1-22a)

\[ C_j = C_{Ao} \frac{T_oP}{TP_o} \left( \frac{\bar{M}_{j/A} + \nu_j x_A}{1 + \varepsilon_A x_A} \right) \]  \hspace{1cm} (1-22b)

Subscript o refers now to the feed conditions.

The volumetric flow rate is given by:
\[ Q = Q_o (1 + \varepsilon_A x_A) \frac{P_o}{PT_o} \]  \hspace{1cm} (1-23)

and total molar concentration is:
\[ C_{tot} = C_{tot,o} \frac{T_oP}{TP_o} \]  \hspace{1cm} (1-24)

Mole fraction of species j is:
\[ y_j = \frac{C_j}{C_{tot}} = \frac{n_{j,o} + \nu_j X}{n_{tot,o} + X \sum_{j=1}^{n} \nu_j} = y_{Ao} \frac{M_{j/A} + \frac{\nu_j}{(-\nu_A)} x_A}{1 + \varepsilon_A x_A} \]  \hspace{1cm} (1-25)
Mass Fraction, \( w_j \)

\[
\begin{align*}
\frac{m_j}{m_{tot}} &= w_{j0} + \nu_j M_j \xi' & \text{(batch)} \\
\frac{\dot{n}Y_j}{\dot{n}_{tot}} &= w_{j0} + \nu_j M_j \xi' & \text{(flow)}
\end{align*}
\]

\( m_j, \dot{n}Y_j \) - mass of j or mass flow rate of j, \((\text{kg})\) or \((\text{kg/s})\)

\( M_j \) - molecular weight of j, \((\text{kg/kmol})\)

The relationship between extent of reaction per unit mass or per unit volume is indicated below.

\[
\xi' = \frac{X}{m_{tot}} = \frac{\xi}{\rho} = \frac{\dot{Y}}{\dot{n}_{tot}} = \frac{\xi}{\rho}
\]

(1-27)

### 1.4 Rate of Reaction & Rate of Reaction of a Species

Rate of reaction is defined as:

\[
R_j = \text{number of moles of species j formed by reaction per unit volume (or other unit measure of the reaction system) and per unit time}
\]

(1-28)

\( R_j \) – rate of reaction of species j

\( R_j > 0 \) – j is a product, rate of formation is positive

\( R_j < 0 \) – j is a reactant, rate of formation is negative.

For a reactant j we can call \((-R_j) > 0\) the rate of disappearance which is positive. For a single reaction of stoichiometry:

\[
\sum_{j=1}^{s} \nu_j A_j = 0
\]

it follows that

\[
\frac{R_j}{\nu_j} = r \quad R_j = v_j r
\]

(1-29)

where

\( r \) – intrinsic rate of reaction is always positive independent of species.

\( R = f (T, C_j, P, \text{activity, etc.}) \). Reaction rate is a function of temperature, composition, pressure, catalyst activity, etc. Empirically, whenever possible we try to represent the reaction rate as a product of a function of temperature, and a function of composition as
indicated by equation (1-30). It is known that the temperature dependence often (always for elementary reaction) can be described by one of the forms indicated by equation (1-31).

\[ R = f_1(T), f_2(C_1) \quad (1-30) \]

\[ f_i(T) = AT^m e^{-E/RT} \]

The Arrhenius form is most commonly used.

\[ f_1(T) = k_o e^{-E/RT} \]

With

- \( k_o \) – frequency factor
- \( E \) – activation energy (J/mol)

The dependence of the rate on concentrations is most often represented by a power law function. At constant temperature, the rate for an n-th order irreversible reaction (\( K \gg 1 \)) then can be written as:

\[ r = k C_1^{\alpha_1} C_2^{\alpha_2} \quad (1-32) \]

where

- \( k = k_o e^{-E/RT} \) – reaction rate constant \([\text{kmol} \cdot \text{m}^{-3} \cdot \text{s}^{-1}]\)
- \( \alpha_1, \alpha_2 \) – reaction order with respect to reactant 1 and 2, respectively
- \( n = \alpha_1 + \alpha_2 \) – overall reaction order

Let us consider the simplest n-th order rate form dependent on a single reactant A.

\[ \overline{r} = k C_A^n \text{ with } k = k_o e^{-E/RT} \quad (1-33) \]

The enclosed Figure 2 indicates the dependence of the rate on temperature at constant composition.
slope = \frac{\ln r_2 - \ln r_1}{\frac{1}{T_2} - \frac{1}{T_1}} = - \frac{E}{R}

\left| \text{slope} \right| = \frac{\ln r_2}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{E}{R}

FIGURE 2: Arrhenius Plot for an n-th Order Reaction

A 25°C temperature rise raises the rate 10 fold for a process with an activation energy of 20 k cal. It raises the rate 1,000 times for a process with activation energy of 60 k cal. To get the corresponding increases in the rate for n = 1 (first order process) we would have to increase the reactant concentration (or pressure) by ten or thousand times, respectively. For a second order process one would have to increase the concentration (pressure) by a factor of 3.2 and 32 in order to get the corresponding increases in the rate. Clearly, the rate of reaction is much more sensitive to temperature than to composition (in most cases).

For a reversible reaction \( \sum_{j=1}^{4} \nu_j A_j = 0 \), an n-th order rate form at constant temperature can be written as:

\[ r = k_1 C_1^{\alpha_1} C_2^{\alpha_2} - k_2 C_3^{\beta_3} C_4^{\beta_4} \]  \hspace{1cm} (1-34)

Order of forward reaction \( n_f = \alpha_1 + \alpha_2 \)

Order of reverse (backward) reaction \( n_b = \beta_3 + \beta_4 \)

At equilibrium \( r = 0 \), so that

\[ \frac{k_1}{k_2} = \left( \frac{C_1^{\beta_3} C_2^{\beta_4}}{C_3^{\alpha_1} C_4^{\alpha_2}} \right)_{eq} = K_c^p \]  \hspace{1cm} (1-35)
with \( p = 1/s \) where \( s \) is an integer and represents the stoichiometric number of the rate limiting step.

\( K_c \) – the equilibrium constant (in concentration units) is given by the following generalized product of reactant and product concentrations:

\[
K_c = \left( \frac{C_3^{v_3} C_4^{v_4}}{C_1^{-v_1} C_2^{-v_2}} \right)_{eq} = \prod_{j=1}^{s} (C_j^{v_j})_{eq}
\]

\( s = 4 \) \hspace{1cm} (1-36)

The thermodynamic equilibrium constant \( K = \prod_{j=1}^{s} a_j^{v_j} \) is related to the Gibbs free energy change for the reaction

\[
-\Delta G_R^o = RT\ln K \hspace{1cm} \Delta G_R^o = \sum_{j=1}^{s} \nu_j \Delta G_{fj}^o
\]

\( a_j \) – equilibrium activity of species \( j \)
\( \Delta G_R^o \) - standard Gibbs free energy change of reaction.

The following relationship holds for gas systems that follow ideal gas law:

\[
K = K_p \frac{-\sum_{j=1}^{s} \nu_j}{P_o} = K_c (P_o) \left( \frac{-\sum_{j=1}^{s} \nu_j}{(RT)^{v_j}} \right)
\]

\( 1-38 \)

where

\( P_o = 1 \text{ atm, most frequently} \)

Now if the Arrhenius form holds for the rate constants

\[
k_1 = k_{10} e^{-E_1/RT} \hspace{1cm} k_2 = k_{20} e^{-E_2/RT}
\]

\( 1-39 \)

then

\[
E_1 - E_2 = \frac{\Delta H_R^o}{s}
\]

\( 1-40 \)

where

\[
\Delta H_R^o = \sum_{j=1}^{s} \nu_j \Delta H_{fj} \hspace{1cm} \text{standard heat of reaction}
\]

\( 1-41 \)

The needed \( \Delta H_{fj}, \Delta G_{Rj} \) - heat of formation and free enthalpy of formation, respectively, are tabulated for all species.
Langmuir-Hinshelwood (Hougen-Watson) Rate Form

Quite frequently the rate form cannot be represented by a product of a rate constant, that has an Arrhenius or similar exponential dependence on temperature, and a power law function of concentrations. In other words the n-th order rate form does not hold. Sometimes a Langmuir Hinshelwood or Hougen-Watson rate form is suggested by theory or found to fit experimental data. A sample L-H rate form is given below.

\[
r = \frac{k \prod_{j=1}^{s} C_{j}^{\alpha_{j}}}{\prod_{i=1}^{R} (K_i + C_i)^{\beta_i}}
\]

(1-42)

In this case

- the order of reaction cannot be defined uniquely
- an activation energy cannot be defined uniquely

For example, if the L-H rate form is as shown below

\[
r = \frac{k_{a} e^{-\frac{E_{1}}{R T}}}{K_{o} e^{\frac{\Delta E}{R T}} + C_{A}}
\]

(1-43)

- at low T, high pressure \( \rightarrow \) apparent order = 0
- at high T, low pressure \( \rightarrow \) apparent order = 1
- at low T \( \rightarrow \) \( E_{\text{apparent}} = E_{1} \)
- at high T \( \rightarrow \) \( E_{\text{apparent}} = E_{1} - \Delta E \)

This is illustrated in Figure 3.
FIGURE 3: Arrhenius Plot for the L-H Reaction

A word of caution about the value of the rate constant is in order. Given $2A + 1B = 2P$ and $r = 0.2C_A^aC_B^\beta$ at some specified temperature $T$, the rate of disappearance of $A$ is given by

$$-R_A = 0.2A C_A^a C_B^\beta$$

Hence, the rate constant for $A$ at the same conditions is 0.4. This is sometimes overlooked because often it is not clearly stated which rate or rate constant is reported. Such errors should be carefully avoided.

Conversion of units come into play when relationship between rates based on various unit measures of the system are required. Often rates expressed per unit area or unit mass are used in heterogeneous systems.

$$\text{rate of reaction} = \frac{\text{change in the number of moles of species } j \text{ caused by reaction}}{(\text{stoichiometric coefficient of } j)(\text{unit measure of the system})(\text{time})}$$
The relationships among these rates are:

\[
\Rightarrow r^v = r^\prime S_g \rho_b = r^\prime \rho_b = r^\prime \varepsilon_b = r^\prime S_{ex} p_b = r^v \frac{P_b}{\rho_b} \quad (1-45)
\]

1.5 Multiple Reactions

Our treatment presented above for a single reaction can readily be extended to multiple reactions.

\[
\sum_{j=1}^{S} \nu_{ij} A_j = 0 \quad i = 1, 2 \cdots R \quad (1-46)
\]

where

S – total number of chemical species.

R – total number of independent reactions.

Stoichiometric requirements yield:

\[
n_j = n_{j,a} + \sum_{i=1}^{R} \nu_{ij} X_i \quad \text{batch} \quad (1-47a)
\]

\[
F_j = F_{j,a} + \sum_{i=1}^{R} \nu_{ij} \dot{X}_i \quad \text{flow system} \quad (1-47b)
\]

where \( X_i \) is the molar extent of the \( i \)-th reaction.

Rate of Reaction of species \( j \) is now obtained by summing the rate of reaction of \( j \) in each reaction.
\[ R_j = \sum_{i=1}^{\nu} \nu_{ij} r_i \] (1 - 48a) so that \[ R = \nu \mu, \quad r = \nu^{-1} \mu \] (1 - 49b)

\( R_j \) - rate of reaction of species \( j \)

\( r_i \) – rate of \( i \)-th reaction

Given a set of \( R \) reactions among \( S \) chemical species one should determine first the \( R \) independent reactions by examining the rank of the matrix of soichiometric coefficients

\[ R = \text{rank } \nu = \text{rank} \left[ \nu_{ij} \right] \] (1-49)

The rank of the matrix of stoichiometric coefficients gives the number of independent reactions.

If the rank is determined by the Gauss-Jordan procedure then the set of independent reactions is readily picked from it.

In a reaction system of \( S \) chemical species with \( R \) independent reactions we need to monitor the change in composition of \( R \) species only. The composition of the remaining \( S-R \) species is given by the \( S-R \) invariants of the system. This implies that we need to know only the rates of \( R \) reactions, the rates of all species can then be obtained.

If we have selected \( j = 1, 2, ...R \) species, then the rates of these species, \( R_j \) for \( j = 1, 2...R \), are given in terms of the rates \( r_i, i = 1, 2, 3, \cdot R \) for the \( R \) reactions. In matrix form this is stated below:

\[ \frac{R}{(Rx1)} = \frac{\nu}{(RxR)(Rx1)} r \] (1-50)

Solve for the \( R \) rates of reaction, \( r_i, i = 1,2...R \)

\[ r = \left( \nu^T \right)^{-1} R \] (1-51)

Then solve for the remaining rates of \( S-R \) chemical species \( R_j, j = R + 1, ...S \)
\[ R_j = \sum_{i=1}^{R} \frac{\Delta_{ij}}{\Delta} R_i = \sum_{i=1}^{R} \frac{\Delta_{ij}}{\Delta} R_i \]  

(1-52)

\[ \Delta = \det \begin{pmatrix} v_{11} v_{12} \ldots v_{ij} \ldots v_{1R} \\ v_{21} v_{22} \ldots v_{ij} \ldots v_{2R} \\ \ldots \ldots \ldots \ldots \ldots \ldots v_{R1} v_{R2} \ldots v_{ij} \ldots v_{RR} \end{pmatrix} \]  

(1-53)

\[ \Delta_{ij} = \det \begin{pmatrix} v_{11} v_{12} \ldots v_{ij} \ldots v_{1R} \\ v_{21} v_{22} \ldots v_{ij} \ldots v_{2R} \\ \ldots \ldots \ldots \ldots \ldots \ldots v_{R1} v_{R2} \ldots v_{ij} \ldots v_{RR} \end{pmatrix} \]  

(1-54)

Similarly

\[ F_j = F_{j,o} + \sum_{i=1}^{R} \frac{\Delta_{ij}}{\Delta} (F_i - F_{i,o}) \quad j = R + 1, R + 2 \ldots S \]  

(1-55a)

\[ n_j = n_{j,o} + \sum_{i=1}^{R} \frac{\Delta_{ij}}{\Delta} (n_i - n_{i,o}) \quad j = R + 1, \ldots S \]  

(1-55b)

To understand fully what this means and how it works consider the following system of \( R' = 3 \) reactions among \( S = 4 \) species

\[ \begin{align*}
2C + O_2 &= 2 CO \quad i = 1 \\
2CO + O_2 &= 2 CO_2 \quad i = 2 \\
2 C + 2O_2 &= 2 CO_2 \quad i = 3 = R'
\end{align*} \]  

(1-56a)

(1-56b)

(1-56c)

and let

\[ A_1 = C, A_2 = O_2, A_3 = CO, A_4 = CO_2 \] so that \( S = 4 \).

First show that there are only two independent reactions \( R = 2 \) (this is rather evident here as the sum of (56a) and (56b) yields (56c)!). Choose the first two reactions and first two species to apply eq (50) and eq (51) to. Then solve for the rates of CO and CO\(_2\) in terms of the rates of C and O\(_2\) using eq (52).

1.5.1 Change in composition in multiple reactions due to reaction, (temperature and pressure change)
The formulas for a single reaction can readily be extended as shown below.

**Molar flow rate (total)**

\[
F_{\text{tot}} = F_{\text{tot, o}} + \sum_{j=1}^{S} \sum_{i=1}^{R} \nu_{ij} \dot{X}_{ij} = F_{\text{tot, o}} + \sum_{i=1}^{R} \nu_{i} \dot{Y}_{i}
\]

(1-57)

\[
\nu_{i} = \sum_{j=1}^{S} \nu_{ij}
\]

(1-58)

**Total molar concentration (ideal gas mixture)**

\[
C_{\text{tot}} = \frac{P}{RT} \quad C_{\text{tot, o}} = \frac{P_{o}}{RT_{o}}
\]

(1-59)

\[
QC_{\text{tot}} = Q_{o}C_{\text{tot, o}} \left\{ 1 + \frac{\sum_{i=1}^{R} \nu_{i} \dot{Y}_{i}}{F_{\text{tot, o}}} \right\}
\]

(1-60)

**Volumetric Flow Rate**

\[
Q = Q_{o} \frac{P_{o} T}{P T_{o}} \left\{ 1 + \frac{\sum_{i=1}^{R} \nu_{i} \dot{Y}_{i}}{F_{\text{tot, o}}} \right\}
\]

(1-61)

**Molar Concentration**

\[
C_{\text{tot, o}} = \frac{P T_{o}}{P_{o} T} \frac{F_{Jo} + \sum_{i=1}^{R} \nu_{i} \dot{X}_{i}}{\sum_{j=1}^{S} \left( F_{Jo} + \sum_{i=1}^{R} \nu_{i} \dot{X}_{ij} \right)}
\]

(1-62)

\[
C_{\text{tot}} = C_{\text{tot, o}} \frac{P T_{2}}{P_{o} T}
\]

(1-63)

**Mole Fraction**

\[
y_{j} = \frac{F_{Jo} + \sum_{i=1}^{R} \nu_{i} \dot{X}_{i}}{F_{\text{tot, o}} + \sum_{i=1}^{R} \nu_{i} \dot{Y}_{i}}
\]

(1-64)

**Mass Fraction**

\[
w_{j} = w_{Jo} + \sum_{i=1}^{R} \nu_{i} \dot{Y}_{i} M_{j} \quad ; \quad \dot{Y} = \frac{\dot{Y}}{n_{\text{tot}}}
\]

(1-65)
Thus, for gas-phase reactions in order to get a linear set of equations between measures of composition and reaction mass fractions should be used.

Additional terminology often used when dealing with multiple reactions is as follows:

Point (relative) yield

\[ y_{P} = \frac{R_{p}}{-R_{A}} = \frac{\text{rate of production of } P}{\text{role of disappearance of } A} \]  

(1-66)

Overall (relative) yield

\[ Y_{P} = \frac{F_{p} - F_{p0}}{F_{A0} - F_{A}} = \frac{\text{moles of product } P \text{ formed}}{\text{moles of } A \text{ consumed}} \]  

(1-67)

Overall Operational Yield

\[ \bar{Y}_{P} = \frac{F_{p} - F_{p0}}{F_{A0}} = \frac{\text{moles of product } P \text{ formed}}{\text{moles of } A \text{ fed to the system}} \]  

(1-68)
Suggested Exercises

1.6 Other Extensions

The definitions introduced in this chapter were used to describe a single or multiple reactions in homogeneous, single phase system that was operated either as a batch or in continuous steady state mode. Extensions can readily be made to semi-batch systems, or to multiphase systems. In the spirit of lifetime learning you should do well to think as to how you could accomplish this. Discuss it among yourselves.

a) Express the following reaction systems in the form

\[ \sum_{j=1}^{s} \nu_{ij} A_j = 0 \quad i = 1, 2 ... R \]

and identify all \( A_j, \nu_{ij}, R \) & \( S \)

a) \( \text{CaCO}_3 = \text{CaO} + \text{CO}_2 \)
b) \( \text{FeS}_2 + 2\text{H}_2 = \text{FeS} + 2\text{H}_2\text{S} \)
   \( \text{FeS} + \text{H}_2 = \text{Fe} + \text{H}_2\text{S} \)

2 For the reaction

\( C_6\text{H}_6 + \text{Cl}_2 = C_6\text{H}_5\text{Cl} + \text{HCl} \)

and the feed rate of

\[ F_{C_6\text{H}_6} = \frac{1 \text{ kmol}}{S} \quad F_{\text{Cl}_2} = 0.5 \text{ kmol} / s \]

a) find the limiting reactant
b) Find the molar flow rates at the outlet of all species at 90% conversion of the limiting reactant.

3 Consider the following reaction at atmospheric pressure (constant pressure) and temperature of 700 K

\( 4\text{NH}_3 + 5\text{O}_2 = 4\text{ NO} + 6\text{H}_2\text{O} \)
Feed: 10% (mole) NH₃, 1-% O₂, 80% N₂ Conversion of limiting reactant 0.95. Feed rate $F_{\text{tot},0} = 0.01 \text{ kmol/s}$.

a) find the limiting reactant  
b) calculate molar flow rates at the exit  
c) calculate molar concentrations at the exit.

4 Consider steam reforming of natural gas  
$\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO}$

At 1300 K, P = 10 atm. Assume both temperature and pressure are constant.  
Feed: 0.01 kmol CH₄/s, 0.02 kmol H₂O/s. Conversion of limiting reactant 85%.

Calculate  
a) $Q/Q_o$ the ratio of exit and feed volumetric flow rate  
b) Molar concentrations of all components at the exit  
c) Mole fractions at the exit  
d) Mass functions at the exit

5. The rate of reaction of SO₃ at a given set of conditions is found to be 0.02 (kmol/m³ reactor s)

a) Find the rates of reaction of SO₂ and O₂ and the equivalent rate of reaction.  
b) If catalyst bulk density is 1.2 (g/cm³), catalyst pellet density is 2.1 (g/cm³), catalyst total surface area is $S_g = 80$ (m²/g), find the rate of reaction expressed per  
a) unit volume reaction mixture  
b) unit volume of catalyst  
c) unit catalyst area  
d) unit catalyst mass

6. Find the number of independent reactions and all the invariants for the system:

a) $\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$  
$2\text{CH}_4 + 3\text{O}_2 = 2 \text{CO} + 4\text{H}_2\text{O}$  
$2\text{CO} + \text{O}_2 = 2\text{CO}_2$
b) \( \text{SiCl}_4 + 2H_2 = \text{Si} + 4\text{HCl} \)
\( \text{SiCl}_4 + H_2 = \text{SiHCl}_3 + \text{HCl} \)
\( \text{SiHCl}_3 + H_2 = \text{SiH}_2\text{Cl}_2 + \text{HCl} \)
\( \text{SiHCl}_3 + H_2 = \text{Si} + 3\text{HCl} \)
\( 4\text{SiHCl}_3 = 3\text{SiCl}_4 + \text{Si} + 2\text{H}_2 \)

7. Suppose that we are conducting reactions described by 6b) at 1400 K and P = 1 atm.

The feed rate is at 600 K, 1 atm and consists of 10\% (mole), \( \text{SiCl}_4 \), 20\% \( \text{SiHCl}_3 \) and 80\% \( \text{H}_2 \).

a) Calculate the equilibrium composition at reaction conditions,

c) Calculate the ratio of molar flow rate at equilibrium and inlet conditions for each species and for total moles.
1. **Stoichiometry**
   
   \[ A + 3B = 2P \] (gases)
   
   a) **Batch** \( V = \text{const}, \ T = \text{const} \)
   
   \[ C_{A_0} = C_{B_0} = 0.1 \ (mol/L); \ C_{P_0} = 0 \]
   
   Find \( x_B, C_A, C_P \) when \( C_B = 0.01 \ (mol/L) \)
   
   b) **Batch** \( P = \text{const}, \ T = \text{const} \)
   
   \[ C_{A_0} = C_{B_0} = 0.1 \ (mol/L); \ C_{P_0} = 0 \]
   
   Find \( x_B, C_A \) when \( C_B = 0.01 \ (mol/L) \)
   
   c) **Flow System** \( P = \text{const}, \ T = \text{const} \)
   
   \[ C_{A_0} = C_{B_0} = C_{P_0} = 0.1 \ (mol/L) \]
   
   Calculate \( C_A, C_B, C_P \) when \( x_B = 0.8 \)

2. **Stoichiometry**
   
   \[ 2A + B = P \] (liquid)
   
   a) **Batch** \( V = \text{const}, \ T = \text{const} \)
   
   \[ C_{A_0} = C_{B_0} = C_{P_0} = 0.1 \ (mol/L) \]
   
   Find \( x_A \) when \( C_A = 0.01 \ (mol/L) \) and calculate \( C_B, C_P \).
   
   b) **Flow System** \( P = \text{const}, \ T = \text{const} \)
   
   Repeat part (a)

3. **Stoichiometry**
   
   \[ 2A + B = P \] (gases)
   
   Repeat parts (a) and (b) of problem 2.
I. Reaction - change in molecular form or content of chemical species due to species – species interactions or due to energy transfer.

Reactor - vessel or space within which chemical reaction is contained.

Reaction Stoichiometry - represents the conservation law of atomic species leading to the mass balance on reaction.

Single Reaction - a reaction system where a single stoichiometric equation accounts for the mass balance.

\[ \sum_{j=1}^{S} \nu_j A_j = 0 \] - stoichiometric equation

\[ \sum_{j=1}^{S} \nu_j M_j = 0 \] - mass balance

\( A_j \) - chemical formulation of j-th species

\( M_j \) - molecular weight of j-th species

\( \nu_j \) - stoichiometric coefficient of j-th species

\( S \) - total number of species present in the system

II. Measures of Reaction Progress

1. Reaction Extent = \( \frac{\text{moles of } j \text{ produced by reaction}}{\text{stoichiometric coefficient of } j} \)

so that

\[ n_j = n_{j_0} + \nu_j \dot{X} \] (1) batch

\( n_j \) (moles of j present) = \( n_{j_0} \) (moles of j originally present) + \( \nu_j \) (moles of j produced by reaction)

\[ F_j = F_{j_0} + \nu_j \dot{X} \] (1a) flow system (steady state)

\( F_j \) (moles of j/unit time), \( \dot{X} \) (moles/unit time)
Limiting Reactant - present in amounts less than required by stoichiometry and limits the reaction extent by having the smallest $\frac{n_{jo}}{-\nu_j}$.

$X_{max}$ - smallest ratio $\frac{n_{jo}}{-\nu_j}$ based on initial mixture for any species $j$ that is a reactant.

By convention we select $j = A$ to indicate the limiting reactant.

2. (Fractional) conversion $= \frac{\text{(moles of } A \text{ reacted)}}{\text{(moles of } A \text{ initially present)}}$

\[
\begin{align*}
\text{batch:} & \quad x_A = \frac{n_{Ao} - n_A}{n_{Ao}} \\
\text{flow (steady state):} & \quad x_A = \frac{F_{Ao} - F_A}{F_{Ao}}
\end{align*}
\]

(3) Relationship between conversion (unitless) and extent (molar)

\[
n_{Ao} x_A = (-\nu_A)X = \text{moles of } A \text{ reacted}
\]

(4) Moles of any other species calculated from conversion of limiting reactant:

\[
n_j = n_{jo} + \frac{\nu_j}{(-\nu_A)} n_{Ao} x_A = n_{Ao} \left( \frac{n_{jo}}{n_{Ao}} + \frac{\nu_j}{(-\nu_A)} x_A \right)
\]

(5) III. Relationship between molar concentration and measures of reaction progress

Definitions

\[
\begin{align*}
C_j &= \frac{n_j}{V} = \text{moles of } j \text{ per volume} & \text{batch} \\
C_j &= \frac{F_j}{Q} = \text{moles of } j/\text{unit time} & \text{flow} \\
C_j &= \text{molar concentration of } j \\
C_{tot} &= \text{total molar concentration} \\
C_{tot} &= \sum_{j=1}^{i} C_j
\end{align*}
\]
Second subscript \( o \) will indicate feed or initial conditions e.g. \( C_{jo} \) molar concentration of \( j \) in feed (or initially).

\[
C_j = \frac{n_{jo} + \nu_j X}{V} = C_{jo} + \nu_j \xi \quad (6)
\]
\[
\xi = \frac{X}{V} = \frac{X}{Q} \quad (7)
\]
\[
C_j = \frac{F_{jo} + \nu_j}{Q} \dot{X} \quad (6a)
\]

Only true if volume of the system (volumetric flow rate) does not change with reaction. Thus, almost always true in liquids.

\[
C_j = C_{A_o} \left( \frac{C_{jo}}{C_{A_o}} + \frac{\nu_j}{(-\nu_A)} x_A \right) \quad (8)
\]
\[
(-\nu_A) \xi = C_{A_o} x_A \quad (9)
\]

In general volume (volumetric flow rate) changes with reaction and we need an additional relation relating the volume to composition, pressure and temperature of the system, i.e. we need an equation of state.

For example, take ideal gases

\[
PV = n_{tot} \quad RT
\]
\[
V = V_o \frac{n_{tot}}{n_{tot,o}} \frac{T}{T_o} \frac{P_o}{P}
\]
\[
n_{tot} = n_{tot,o} + X \sum_{j=1}^{S} \nu_j; \quad \frac{n_{tot}}{n_{tot,o}} = 1 + \frac{\left( \sum_{j=1}^{S} \nu_j \right) X}{n_{tot,o}}
\]

Coefficient of Expansion = \( \frac{\text{increase in total moles caused by complete reaction of limiting reactant}}{\text{total moles initially}} \)

\[
\varepsilon_A = \frac{X_{max} \sum_{j=1}^{S} \nu_j}{n_{tot,o}} = \frac{\sum_{j=1}^{S} \nu_j}{y_{Ao} (-\nu_A)} \quad (10)
\]

Therefore, in batch (variable volume)
\[
\frac{V}{V_o} = \frac{T}{T_o} P_o \left( 1 + \frac{\sum_{j=1}^{S} v_j}{n_{tot,o}} \dot{X} \right) = \frac{T}{T_o} P_o \left( 1 + \varepsilon_A x_A \right)
\]

\[
\frac{Q}{Q_o} = \frac{T}{T_o} P_o \left( 1 + \frac{\sum_{j=1}^{S} v_j}{F_{tot,o}} \dot{X} \right) = \frac{T}{T_o} P_o \left( 1 + \varepsilon_A x_A \right) \quad \text{in flow (s.s.)}
\]

\[
C_j = \frac{(F_{j_o} + v_j \dot{X})}{Q_o \left( 1 + \frac{\sum_{j=1}^{S} v_j}{F_{tot,o}} \dot{X} \right)} \frac{T_o}{P_o}
\]

or

\[
C_j = C_{Ao} \left( \frac{C_{j_o} + v_j}{C_{Ao} - v_A} \right) \frac{x_A}{1 + \varepsilon_A x_A} \frac{P}{P_o} \frac{T_o}{T}
\]
LECTURE 1D. REACTIONS AND REACTORS

Before we start developing a systematic approach to the treatment of various reaction systems it is beneficial to learn some pertinent terminology and to get exposed to the variety of systems that one might encounter in practice.

The objective of this chapter is to define chemical reactions and present possible bases for classification of reaction systems. It also exposes the reader to some industrially important reactions and makes him aware of the basic reactor types used in practice.

Upon reading of this chapter you should be able to:

i) define chemical reaction
ii) classify reaction systems
iii) list commonly used reactor types in industry
iv) define hourly space velocity and reactor space time
v) know where to look for some additional information on processes and reactor design.

1.1 Chemical Reactions

Whenever molecules of an identifiable chemical species are transformed to a new form and/or different atomic content we say that a chemical reaction occurred. From a chemical reaction engineering point of view a chemical reaction takes place only when a detectable number of molecules of one or more chemical species undergo a change i.e. assume a new identity. This new identity can be the result of a change in the number and type of atoms in the molecules, or it can be caused by a variation in the configuration of molecules while preserving their original atomic content. For example, a change in molecular form but not content occurs in isomerizations, e.g.

\[ CH_3 - CH_2 - CH = CH_2 \Leftrightarrow CH_3 - CH = CH - CH_3 \]  (1)

A change in both molecular content and form occurs in decomposition reactions e.g.

\[
\begin{align*}
\text{cumene (isopropyl benzene)} & \quad \text{benzene} + C_3H_6 \\
\end{align*}
\]

or synthesis (combination) reactions such as saponification, e.g.
\[
\text{NaOH} + CH_3COOC_2H_5 = CH_3COONa + C_2H_3OH
\]

Those chemical species that undergo the reaction transformation we call reactants; species resulting from reaction are called (reaction) products.

By a reaction system we mean a volume in Euclidian space containing a certain mass of identifiable chemical species among which reactions occur. We attempt to describe the reaction system by writing down the pertinent formulas for the reactions that occur.

Various classifications of reaction systems are possible. One may distinguish them based on the energy form associated with the reactions in the system. Reactions can be induced by (or produce) thermal energy (thermal reactions), photochemical energy (photochemical reactions), electrical energy (electrochemical reactions), etc. For example, decomposition position of limestone to lime is a thermal reaction

\[
CaCO_3 = CaO + CO_2
\]

while decomposition of ozone can be photochemically induced

\[
2O_3 + h\nu = 3O_2
\]

The chlor-alkali process is a well known example of electrochemical reactions.

\[
2NaCl + 2H_2O + \text{electric - current} = Cl_2 + 2NaOH + H_2
\]

At the moment we are contented to write photo-chemical and electrochemical reactions in a simplified manner by indicating only that either emission of photons or passage of an electric current are linked to reaction progress. More accurate description will follow later.

Another basis for classification would be the presence or absence of a catalyst (i.e. catalytic versus noncatalytic systems). Classification can also be done based on the type of reaction occurring in the system (i.e. chemical, biochemical, polymerization, biological, etc. While all of the above approaches are useful, we will constrain ourselves at the moment to classify reaction systems based on two measures:

i) the number of reactions occurring in the system,

ii) the number of phases present in the system.

Within each of these two classifications we can further group reaction systems based on the criteria discussed above and talk about thermal, photochemical, biochemical and other processes, catalytic or noncatalytic reactions, etc. Another important consideration is whether the reaction mixture behaves ideally or nonideally from the thermodynamic point of view.
When we consider reaction systems from the standpoint of the number of reactions occurring we mean the number of stoichiometric relations needed to describe the conservation of all atomic species in the system (more about that in the next chapter). Hence, we can distinguish single reaction systems, multiple reaction systems and complex reaction systems. From the standpoint of the number of phases involved we will talk about homogeneous (single phase) and heterogeneous (multiphase) systems. We will consider a system to be heterogeneous even when all reactants and products are present in a single phase but the presence of another phase is necessary for the reaction to proceed (e.g. solid catalyst). We will show later, however, that such heterogeneous systems can under some circumstances be treated as pseudo-homogeneous.

In case of a single reaction, a single equation describes species conservation in the system as will be shown in the next chapter. There are many industrially important single reaction systems. Classic examples in production of commodity chemicals are sulfur trioxide (sulfuric acid) production and synthesis of ammonia. Sulfur trioxide is made by oxidation of $SO_2$ on an alumina supported vanadium pentoxide or alumina supported platinum catalyst at several hundred degrees centigrade and slightly above atmospheric pressure.

$$2 \text{SO}_2(g) + \text{O}_2(g) \xrightarrow{\text{cat.}} 2 \text{SO}_3(g) \quad (4)$$

Sulfuric acid production is large (over 35 million tons per year) and most of it is used in production of other chemicals, phosphoric acid manufacture, cellulose decomposition and petroleum refining.

Ammonia is the starting point for the production of nitrogen based fertilizers. Over 75% of the ammonia produced is used to make fertilizers. It is synthesized from hydrogen and nitrogen at very high pressures and temperatures.

$$3 \text{H}_2(g) + \text{N}_2(g) \xrightarrow{\text{cat.}} 2 \text{NH}_3(g) \quad (5)$$

Both of the above single reaction systems are heterogeneous (why?). The second one ($\text{NH}_3$ synthesis) is a two phase system (gas-solid catalyst) while the first one ($\text{SO}_2$ oxidation) is actually a three phase system (gas-liquid-solid) since $V_2\text{O}_5$ forms a melt which fills the alumina pores at reaction conditions. If we wanted to calculate equilibrium conditions for the above two systems we could treat the first system as ideal while the second one, due to high pressure, must be considered nonideal. Hence, we see that chemical thermodynamics is an important and needed tool in characterizing the number of phases and equilibrium behavior of reaction systems.

An example of a homogeneous single reaction in the gas phase is the thermal decomposition of acetaldehyde.

$$\text{CH}_3\text{CHO}(g) = \text{CH}_4(g) + \text{CO}(g) \quad (6)$$
Esterification is an example of a single, homogeneous liquid phase reaction promoted by a homogeneous catalyst \((HC\ell + H_2O)\):

\[
CH_3COOH + C_2H_5OH \xrightarrow{\text{cat.}} CH_3COOC_2H_5 + H_2O \quad (7)
\]

Silane decomposition to make silicon for semiconductor applications is an example of a single, gas-solid noncatalytic reaction:

\[
SiH_4(g) = Si(s) + 2H_2(g) \quad (8)
\]

Production of hexamethylene diamine (HMDA) by adiponitrile (ADN) hydrogenation is a single, catalytic, heterogeneous (gas-liquid-solid) reaction:

\[
NC(CH_2)_4 CN(\ell) + 4 H_2(g) \xrightarrow{\text{Raney Ni}(s)} H_2N(CH_2)_6 NH_2(\ell) \quad (9)
\]

HMDA is polymerized with adipic acid to form nylon 6,6.

**Multiple reaction systems** are those described by more than one well-defined stoichiometric equations.

Partial oxidation of ethylene to ethylene oxide (processed to ethylene glycol for antifreeze or polyester fibers) over a silver catalyst is an example of multiple, heterogeneous (gas-solid) reactions:

\[
C_2H_4(g) + \frac{1}{2} O_2(g) \xrightarrow{\text{cat.}} C_2H_4O(g) \quad (10a)
\]

\[
C_2H_4(g) + 3 O_2(g) \xrightarrow{\text{cat.}} CO_2(g) + 2H_2O(g) \quad (10b)
\]

Chlorination of benzene is an example of multiple, heterogeneous (gas-liquid) noncatalytic reactions:

\[
C_6H_6(\ell) + Cl_2(\ell) = C_6H_5Cl(\ell) + HC\ell(\ell) \quad (11a)
\]

\[
C_6H_5Cl(\ell) + Cl_2(\ell) = C_6H_4Cl_2(\ell) + HC\ell(\ell) \quad (11b)
\]

\[
C_6H_4Cl_2(\ell) + Cl_2(\ell) = C_6H_3Cl_3(\ell) + HC\ell(\ell) \quad (11c)
\]

Production of polyethylene terephthalate (mylar or dacron) from dimethyl terephthalate and ethylene glycol by a two step method is an example of heterogeneous (gas-liquid) catalytic multiple reactions:
Polymerization of ethylene is an example of multiple, catalytic, heterogeneous (gas-solid) reactions.

\[ nC_2H_4 = (C_2H_4)_n \]  

We will call complex systems those for which it is impractical to identify all the species in the feed stream and/or product stream. Hence, the exact reactions taking place cannot be written and one is forced to lump together species that are alike (by molecular weight or chemical behavior) and make mass balances on these lumps. Examples of complex reaction systems are: catalytic hydrocracking of petroleum, cell growth, coal gasification, etc. Catalytic hydrocracking reduces high molecular weight hydrocarbons (HMW) to lower molecular weights (LMW).

\[ (HMW) + nH_2 \rightarrow LMW \]  

In biomass formation an organic substrate (S) is used to produce cell mass (CM) plus metabolic wastes (MW).

\[ S + O_2 \rightarrow CM + MW \]  

In steam gasification of coal mainly synthesis gas is produced:

\[ coal + nH_2O + heat \rightarrow CO + H_2O + other \]  

We note that, at the moment, we are characterizing complex reaction systems imprecisely and equations (14) – (16) are not even proper stoichiometric statements, rather they are only indicative of the key feature of the system.

Several points should be made here. Our classification of reaction systems according to the number of reactions and number of phases involved is helpful in assessing what approach to use in quantifying transport-kinetic interactions in a system. Clearly, thermodynamic information is essential in properly assessing the phase information regarding a particular system. The classification system is not perfect and may need to evolve further to properly encompass reactions in plasmas, molecular beams, etc.
Our definition of a single reaction does not necessarily coincide with the point of view expounded by chemists. For example, decomposition of $SiH_4$ may involve more than 130 reactions among which at least about 25 among a number of species are important enough to determine the course of the overall reaction. However, at any point in time there are only three species ($SiH_4, Si, H_2$) that are present in comparable concentrations. All other species have concentrations that are many orders of magnitude lower. Hence, the atomic mass balance can be closed, i.e., conservation of atomic species can be accounted for with small error if we only consider these three species and a single relation tying them. The other species present in infinitesimal amounts are irrelevant for the stoichiometry of the system but could be important in deciphering its mechanism. We will define these two terms in the next chapter.

### 1.2 Chemical Reactors

The vessels (or spaces) within which chemical reactions take place are called reactors. A variety of reactor types have been designed over the years for handling of homogeneous liquid, homogeneous gas, heterogeneous gas-liquid, gas-solid, or gas-liquid-solid reactions. Some examples are illustrated in Figure 1.

The variety of reactor designs used is certainly overwhelming and only a small sample is shown or mentioned here. Nevertheless, a systematic approach to reactor classification is possible based on several criteria such as:

i) batch, semi-batch, or continuous processing

ii) number of phases that need to be contacted and their nature

iii) contacting or mixing pattern

For batch or semi-batch processing of homogeneous liquid or heterogeneous gas-liquid (or even liquid-solid) systems various types of autoclaves are used. These are turbine mixed vessels that can operate at high pressures. Liquid reactants plus homogeneous catalyst are added to the vessel which is heated to the desired reaction temperature. After reaction completion the contents are pumped out. Solid catalyst can be added to these systems to form liquid slurry. Typical particle size used would be in the $10 – 300 \mu m$ range. Gas reactant can be sparged through the vessel while keeping vessel pressure constant in a semi-batch operation.

Semi-batch fermentors operate on the same principle but do not require high pressure, usually use more gentle mixing and besides continuous gas addition may employ continuous removal of gaseous reaction products.

Continuous processing of homogeneous gaseous or liquid systems can be done in various types of tubular vessels filled with internals to promote the desired level of mixing. Liquids can also be processed in stirred vessels. Mixing of reactants prior to entering the reactor section or during reaction is the key variable affecting the performance of these reactors.

Reactions between gases are mainly carried out in continuous operation. When these reactions are fast, the reaction zone is small (e.g. flame in $C\ell_2$ combustion, electric arc in $C_2H_2$
production from \( CH_4 \) and the reactor contains the reaction zone and accommodates the heat transfer requirements. Large units and autoclaves may be necessary in some applications (e.g. \( C_2H_2 \) decomposition to acetylene black).

Liquid phase reactions are mainly carried out batchwise. For semi-batch or continuous operation stirred vessels, autoclaves or tubular reactors with static mixers can be used.

Gas-liquid reactors can be divided into several types depending whether gas or liquid or both form a continuous phase. In a wetted wall column or packed bed with counter-current gas-liquid flow both phases are continuous. Liquid forms a discrete phase in a spray reactor while gas is the discrete phase in a mechanically agitated vessel, bubble column packed bed with gas-liquid cocurrent upflow, venture contactor, etc.

Reactions between gases and solids are conducted in a semicontinuous (batch solids-continuous gas) or continuous manner. Reactors used consist of packed beds (fixed beds) of solids, fluidized beds, and moving beds of solids. Rotary kilns, gas-solid transport reactors, cascading solids are some of the examples of moving beds. In specialty applications such as semiconductor and optical fiber production new types of gas-solid reactors are emerging.

Gas-liquid-solid reactions are normally conducted with continuous gas-liquid flows. Typical reactors are agitated slurry reactors, slurry bubble columns, ebulated beds of solids, packed beds with cocurrent gas-liquid downflow (trickle-beds).

We will consider later on how reactors can be classified based on flow patterns that they try to promote. In some fast mixing of the inlet stream with reactor contents is promoted, in others inlet streams and reactor contents close to the exit do not mix at all.

An article by Professor S.M. Walas (Chemical Reactor Data in Chemical Engineering, October 14, 1985, pp 79-83) illustrates the reactor types used in 102 industrially important chemical processes. Operating conditions and type of catalyst used are also listed as well as either apparent residence time or space velocity. In order to interpret the table properly it is necessary to understand the following definitions of space velocity that are used in the table:

\[
GHSV \ (h^{-1}) = \left( \frac{\text{volume of feed gas}}{\text{h}} \right) / \left( \frac{\text{volume of reactor or catalyst}}{\text{h}} \right)
\]

\[
LHSV \ (h^{-1}) = \left( \frac{\text{volume of feed liquid}}{\text{h}} \right) / \left( \frac{\text{volume of reactor or catalyst}}{\text{h}} \right)
\]

\[
WHSV \ (h^{-1}) = \left( \frac{\text{mass of feed liquid}}{\text{h}} \right) / \left( \frac{\text{mass of catalyst in reactor}}{\text{h}} \right)
\]

In the above definitions volumetric flow rates are evaluated at standard conditions of 15° C (60° F) and 1 atm (14.7 psia).

When the entry in the table is (apparent) residence time, in time units, the definition of it is
(apparent) residence time = \frac{(Reactor \ (or \ catalyst) \ volume)}{(Volumetric \ Flow \ Rate \ at \ Feed \ Conditions)}

We will see later that the apparent residence time so defined is really the space time of the reactor. It is a measure of how long on the average the feed is exposed to the reaction environment. Space velocity is proportional to the reciprocal of the space time as defined above. The larger the space velocity the smaller the residence time in the reactor.

To our knowledge the information presented by Walas, is the only attempt to gather in one place this kind of useful information. Nevertheless, the information should be used with caution since it is not always clear whether catalyst or reactor volume was used in reporting space velocity or residence time. For a typical bed porosity of 0.5 this may mean a difference of a factor of 2 in these values, if the wrong volume is assumed.

1.3 Systematic Approach to Studies of Reaction Systems and Reactors

In the chapters that follow we will develop the relationships necessary for a unified, systematic approach to the variety of reaction systems illustrated earlier. In order to do that we have to start from the simplest case and gradually develop the capability to handle the most complex case. The simplest situation is that of a homogeneous (single phase) reaction system with a single reaction occurring in a thermodynamically ideally mixture. Sulfur dioxide oxidation at atmospheric pressure fits this category if treated as a pseudo homogeneous system. A complex case would involve a multiphase system (at least three phases) with multiple reactions. Therephtalic acid production fits into this category. Thus, we can depict the following tree for the level of difficulty in treating reaction systems.

<table>
<thead>
<tr>
<th></th>
<th>Multiple</th>
<th>Nonideal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Three or more</td>
<td>Single</td>
<td>Ideal</td>
</tr>
<tr>
<td>Two</td>
<td>Multiple</td>
<td>Nonideal</td>
</tr>
<tr>
<td></td>
<td>Single</td>
<td>Ideal</td>
</tr>
<tr>
<td>Single</td>
<td>Multiple</td>
<td>Nonideal</td>
</tr>
<tr>
<td></td>
<td>Single</td>
<td>Ideal</td>
</tr>
</tbody>
</table>

↑ No. of Phases Present  ↑ No. of Reactions  ↑ Thermodynamic Behavior

In the next chapter we introduce the relationships necessary to deal with homogeneous systems. We will follow later with relations required to handle heterogeneous systems.

In our systematic approach to reactor analysis we will introduce the concept of ideal reactors for homogeneous systems, consider which of these concepts can be realized in practice and how to assess performance of real reactors. Later we extend these concepts to heterogeneous systems.