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Thermodynamic Analysis in Chemical Process and Reactor Design

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Introduction

Thermodynamic analysis is a very useful tool for the industrial chemist, catalyst chemist, process designer and the chemical reactor designer. It is not only useful for understanding existing processes; if properly used it can offer stimulating insight into the design of new processes and indicate ideas for improvement of old ones. It can also serve as a guide for future research and development in the areas of catalysts, process design and reactor design.

The suggestion that considerations based on the second law of thermodynamics should be important in chemical reator and process design is not new. Denbigh (17) emphasized it many years ago, and quite a number of papers dealt with the subject since then [2,5,19,29,38,44,46,47,48,50,52,55, 58,59,62]. However, if one looks at actual practice, one cannot escape the feeling that thermodynamic considerations have been under-utilized in these areas. In this review I try to show that thermodynamics can play a much more significant role than it has until now and that the field of thermodynamics as applied to design has a number of important, outstanding problems.

In order to properly utilize the power of thermodynamic analysis, one must go beyond conventional second law or energy analysis [10,15,18,19,23, 45,60]. Although valuable as tools, these analyses do not give the engineer direct practical hints on how to improve a design, or on what alternatives to research. One of the main causes of this in chemical process design is that the real restrictions on reactor conversion derive from sources other and more severe than the second law. Very seldom is the second law the tightest constraint. Usually it is overshadowed by constraints of available technology [38,50,52]. These, however, have consequences that can avail themselves of thermodynamic analysis as well [50,52]. For example, consider power plant design. For most conventional fuels, standard second law analysis says little; the available free energy of methane and most fuels is very close to its lower heating value [3,4] and, as a result, the theoretical limiting thermal efficiency of such a power plant is 100%. However, thermodynamics has more subtle uses. For example, in order to fabricate a steam power plant from carbon steel as opposed to a more expensive alloy, one must design it to operate at 650°C. Carnot's Law gives a maximum efficiency at 650°C of 67.7%, thereby estimating the penalty of this decision.

The ideas reviewed below employ thermodynamic analysis to understand and to try to overcome inefficiencies and constraints in present technology even though these constraints may not all be thermodynamic in nature. Only a thorough understanding of these constraints will lead to a better technology. I illustrate this point with some examples, which I do not intend to be exhaustive.

Section II deals with energy utilization and thermal efficiency, the focus of most previous work. With a simple example, Section III illustrates the much broader applicability of thermodynamic analysis of process constraints towards improving processes.

Section IV shows how thermodynamic analysis can be a powerful tool in the analysis and modelling of complex chemical reactions. Section V approaches the problem of which information one needs in order to model a complex reaction system; it considers both the viewpoint of the chemical reactor designer and that of the chemical process developer. Section VI explains conversion limitations dictated by thermodynamics for a given catalyst and applies this to screening procedures for new catalysts.

In Section VII we continue this line of thought by considering applications to chemical process development and design. This entails suggesting ways of circumventing the thermodynamic constraints imposed by catalytic properties. Shape selective zeolite catalysts, as illustrated in Section VIII, can modify thermodynamic constraints, thereby introducing new avenues in the design of catalysts. Finally, in Section IX we discuss some of the challenges for future research.

II. The value of heat in a chemical plant

The simplest important application of second law analysis is to value the heat content of a process stream. In order to illustrate the pitfalls of such an analysis, we consider an example used by Denbigh (17) and several other authors [38,46,47], the production of nitric acid from ammonia. Denbigh's reactor efficiency in recovering the free energy change of reaction as useful heat is only 40%. How can we use this information to improve the process?

Nitric acid is usually produced by oxidizing ammonia to nitric oxide, a very exothermic step, followed by further oxidation and hydrolysis.

$$NH_2 + (\tfrac{5}{4})O_2 \dashrightarrow NO + 1.5H_2O \;;\quad \Delta G^{o}_{298} = -55.8\ \frac{kcal}{mole}\ ,\ \Delta H^{o}_{298} = -53.5\ \frac{kcal}{mole} \qquad (1)$$

Note that $\Delta H^{o} < \Delta G^{o}$. Standard reactor conditions provide no practical way of fully recovering the free energy change of the reaction; only an electrochemical cell can accomplish this. The best one can do in a chemical reactor with an exothermic reaction is to fully recover the heat of reaction at the temperature of the reaction. The thermodynamic value of this recovered heat is given by its free energy which is

$$\Delta G \text{ (heat released)} = \Delta H \left(1 - \frac{T_o}{T_R}\right) \quad , \qquad (2)$$

where T_o is the temperature of the environment and T_R is the temperature of the reactor.

As $\Delta H_o < \Delta G_o$, the free energy cannot be recovered in a conventional, non-electrolytic chemical reactor.

The relation between ΔH and ΔG has important implications for chemical process design. In an exothermic reaction we recover the free energy released by the reaction as reaction heat. It is obvious that in a spontaneous reaction the free energy value of the heat released cannot be larger than the change in free energy ΔG due to the reaction itself, i.e.

$$\Delta H(1- {T_o}/T_R) \leq \Delta G \qquad (3)$$

If T_R gives equality in Eq. 3 then the reaction runs almost reversibly and the heat recovery is optimal in terms of its thermodynamic value. We will call this temperature T_R^*. Running the reaction at a higher temperature means that the free energy value of the heat of reaction recovered is larger than the ΔG of the reaction; this difference must be externally supplied. For example, if the process depletes moles, the designer can supply free energy by compressing the products in order to avoid conversion limitations. And the way to generate the additional free energy is by an external separation process (31).

Analogously, when the reaction is endothermic, T_R should be larger than T_R^*. Since in our example, $\Delta G^o > \Delta H^o$, there is no value of T_R^* which gives equity in Eq. 3. In other words, there is no optimal temperature; recovery of ΔG theoretically continues to increase with increasing temperatures. However, practical material constraints place an upper bound on the temperature at which real catalysts operate. Therefore, in practice, one oxidizes ammonia at 1000°C, which is close to the maximum temperature that has been achieved in catalysts, although thermodynamically one would prefer to go higher.

Other considerations also play a role. In this example, it turns out that the paramount free energy recovery constraint derives not from the catalyst, but rather from the cost of transferring heat above 650°C. The standard way to recover the free energy of the heat is the steam cycle, which has a maximum temperature of 650°C. The process as designed (with catalyst and reactor as described), allows maximum practical recovery of the reaction's free energy. Thus, thermodynamic analysis can be misleading when not put in the context of current design practice.

The thermodynamic value of the heat of a process stream is a strong function of the specific plant condition and of current design practice. For example, if a process requires heat at 550°C, yet provides no streams capable of transferring that heat, then the value of that heat is that of the free energy of the fuel, and is the same value as heat at 650°C or higher.

In conventional exergy analysis the thermodynamic value of a heat stream is given by Eq. (2). This can be misleading because in a plant the value of heat recovered is related to the design practice of the plant, i.e., it is the cost of heat inputs. At higher temperatures, say, 800°C, this cost is not due to a higher thermodynamic value, but rather to the expense of transferring heat at the higher temperature. Similarly, excess heat at low temperature, say 200°C, has no value if it cannot be used in the plant because there is no cost effective technology for converting it to power.

In the same spirit of putting thermodynamic analysis of a process in a design context, Hottel [30] has ranked fossil fuels for a boiler in terms of thermal efficiency, based on actual design practices of boilers instead of ΔG. Linhoff [38] has used a similar approach very effetively to look at the methodology of improving the energy recovery in heat transfer networks [38,39,40,41,61,62]. Design analyses can proceed from the perspective of current design practice or from that of coming improvements in technology. Thermodynamic analysis must always be put into the changing context of design practice and available technology.

Thermal efficiency strongly influences the cost of a process [55}. To make improvements one can either improve the energy recovery of existing processes or one can find the underlying reasons for the inefficiencies and restructure the process to eliminate them. The latter is thermodynamic analysis' niche. Our aim below is to illustrate this for chemical reactor and chemical process design.

III. Analysis of process constraints

We begin our discussion of thermodynamic analysis applied to chemical reactor modelling and design with an example, the production of methane from coal, which has been studied in great detail [52]. The overall reaction of methane formation from carbon is

$$2C + 2H_2O \text{ (liq.)} \dashrightarrow CH_4 + CO \qquad \Delta G^o_{298} = 6.9 \frac{\text{kcal}}{\text{mole}} \ , \qquad \Delta H^o_{298} = 24.65 \frac{\text{kcal}}{\text{mole}} \qquad (4)$$

Since this reaction has a positive ΔG, it can illustrate how catalytic processes can achieve an increase in free energy.

In principle, the minimum energy requirement is ΔG = 6.9 kcal/gmole which one must supply in some manner. For example, ideally one could carry out the process in an irreversible electrolytic cell at room temperature. The process would absorb the heat from the surroundings at no thermodynamic penalty. Alternately, one could employ a separation process coupled to compression. In the hypothetical process of Fig. 1, carbon reacts with water vapor at room temperature. A semipermeable membrane separates the methane formed, which is then compressed to one atmosphere. The theoretical work of the compression required is exactly equal to ΔG of the reaction.

In reality, neither a catalyst promoting this reaction nor such a semipermeable membrane exists. Most real separation processes have efficiencies of less than 10%. It is therefore preferable to generate the free energy increase by supplying the heat to the process. Again, one faces a problem stemming from Eq. (3). In order to carry out an endothermic reaction with a

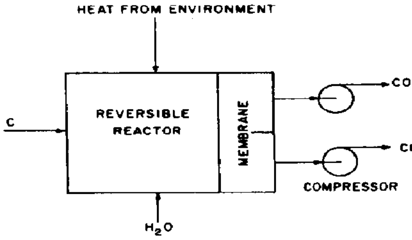


Figure 1 Hypothetical reversible SNG process

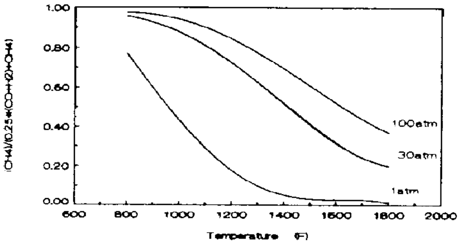


Figure 2 Equilibrium yields of methane in steam gasification of carbon
Yield given as fraction of methane obtained at global equilibrium relative to the total yield of CH_4 if CO, H_2 and CO_2 are converted to CH_4 (4 moles of syngas CO + H_2 yield one mole of CH_4)

positive ΔG in a reactor with high conversion, the endothermic heat of reaction supplied to the process must have a sufficiently high free energy relative to the surroundings to supply the difference in free energy between the feed and the product. Using Eq. (2) one can write

$$\Delta H(1 - \frac{T_o}{T_R} \le \Delta G \quad . \qquad (5)$$

If the specific heat of the reactants is equal to that of the product ΔH in Eq. (5) is approximately ΔH_o.

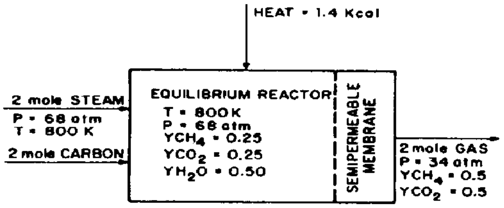


Figure 3 Hypothetical equilibrium reactor for methane production

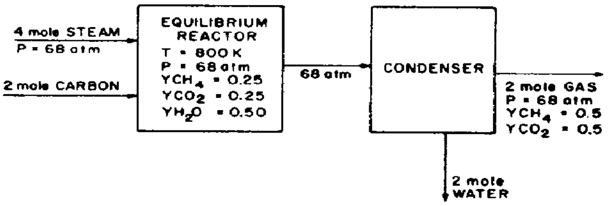


Figure 4 Catalytic gasifier with condensation of steam

A process for converting coal to methane by reacting it with liquid water satisfying (5) could proceed at a reasonably low temperature (T_R > 145°), if such a catalyst existed. Moreover, the only catalysts that exist promote the reaction of carbon not with water but rather with steam. The reactions occurring are

$$2H_2O_{(liq)} \dashrightarrow 2H_2O_{(g)} \ ; \qquad \Delta H^o_{298} = +\ 21.0\ \frac{\text{kcal}}{\text{mole}} \quad , \ \Delta G^o_{298} = +4.1\ \frac{\text{kcal}}{\text{mole}} \qquad (6a)$$

$$2C + 2H_2O_g \dashrightarrow CH_4 + CO_2 \qquad \Delta H^o_{298} = +\ 3.65\ \frac{\text{kcal}}{\text{mole}} \quad , \ \Delta G^o_{298} = +2.8\ \frac{\text{kcal}}{\text{mole}} \qquad (6b)$$

Using steam generates an overall increase in free energy (Eq. 4) in the two step process while the ΔG of the reaction itself has decreased from 6.9 to 2.8 kgcal/gmole.. The larger increase in free energy (4.1 kgcal/gmole) occurs during the steam generation. However, another problem arises from Eq. (66): unlike Eq. (4) where ΔH which gave rise to a low T^*_R, here, T^*_R takes the impractical value of 1500°K.

Methane is unstable above 1300°K and decomposes to carbon and hydrogen. In addition, above 800° carbon reacts with steam yielding CO and H_2 in addition to methane. The reactions giving rise to formation of CO and H_2 are highly endothermic and have a large increase in free energy:

$$C + H_2O \dashrightarrow CO + H_2 \ ; \qquad \Delta G^o_{298} = 21.8\ \frac{\text{kcal}}{\text{mole}} \quad , \ \Delta H^o_{298} = 31.4\ \frac{\text{kcal}}{\text{mole}} \qquad (7)$$

$$CO + H_2O \dashrightarrow CO_2 + H_2 \ ; \qquad \Delta G^o_{298} = 6.9\ \frac{\text{kcal}}{\text{mole}} \quad , \ \Delta H^o_{298} = -9.5\ \frac{\text{kcal}}{\text{mole}} \qquad (8)$$

In the absence of a catalyst, these reactions are favored over reaction (6b). Methane is formed by the reaction:

$$CO + 3H_2 \dashrightarrow CH_4 + H_2O \ ; \qquad \Delta G^o_{298} = 34.0\ \frac{\text{kcal}}{\text{mole}} \quad , \ \Delta H^o_{298} = -49.3\ \frac{\text{kcal}}{\text{mole}} \qquad (9)$$

which also requires a catalyst.

One way to avoid this pathway is to find a catalyst which, as yet does not exist, that selectively promotes direct formation of reaction (6). Present catalysts, such as potassium carbonate, do not promote reaction (6b),but rather (7),(8) and (9). Another approach comes into play when a global equilibrium condition exists that favors the desired product. Then, a desirable catalyst is one that promotes global equilibrium. Let us explain. Global equilibrium yields of methane as a function of temperature and pressure appear in Fig. 2. Since one mole of CH_4 requires 4 moles of syngas, we express this yield by the ratio $CH_4/[CH_4 + 0.25(CO+H_2)]$. At temperatures below 800°K, the product is mostly methane, which leads one to conclude that only reaction (6) proceeds appreciably. However, if the temperature is much less than T^*_R, the free energy of the heat of reaction is less than ΔG; one needs a separation process to create the difference in free energy to assure high conversion. In theory, one could create the ΔG by separating the CH_4 and CO_2 from the steam by a semipermeable membrane, as shown in Fig. 5. The incremental free energy would come from the difference in pressure between the products and the steam in the feed. In practice, however, one achieves the separation by condensing the steam (Fig. 4). This is simple yet inefficient because it does not allow cost efficient recovery of the heat of vaporization of the excess steam diluted by the product. Nevertheless, even at 25% steam conversion, the efficiency and cost of such a process would still be a major improvement over present technology.

Thermodynamic analysis indicates the type of catalyst required. Regrettably, neither a catalyst that directly promotes reaction (6) nor one that promotes global equilibrium at low temperature (below 800°K) exists. What do exist are catalysts which operate close to (1000°K) and generate large amounts of H_2 and CO. Exxon has developed a process that simulates the process in Fig. 5. If one could separate CH_4 and CO_2 from the reactor by a semipermeable membrane there would be no net formation of CO and H_2, and the process could be equivalent to production of CH_4 and CO_2 alone. Exxon's process first adsorbs the CO_2 in a solvent, separates CH_4 cryogenically (Fig. 6), and recycles CO and H_2. However, Exxon's cost of separation is high enough to render its advantage over conventional technology quite small. (Fig.7)

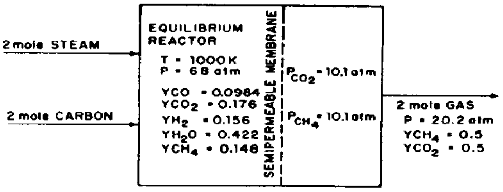


Figure 5 Hypothetical gasifier with semipermeable membrane
Steam reacting with carbon reaching global equilibrium

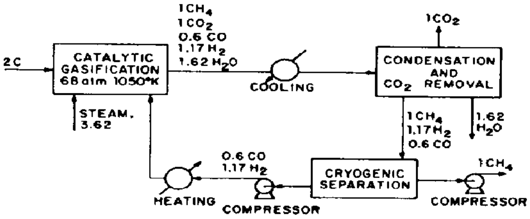


Figure 6 Schematic flowsheet for Exxon catalytic SN process

In the conventional technology, coal gasification with steam at high temperatures generates CO and H_2 which are converted over a low temperature catalyst to methane. The thermal and second law efficiency is much lower than in our process because the first step has a much higher ΔH than reaction (6b), even though this ΔH is later recovered in the methanator at low temperature. In theory, one could run all steps reversibly and transfer heat from lower temperatures to higher temperatures by heat pumps. Since this is impractical, the actual overall process has an efficiency of less than 70%.

This low overall thermal efficiency, rather than deriving from hard thermodynamic constraints, is a thermodynamic consequence of the lack of a suitable catalyst or efficient membranes. While thermodynamic analysis can direct improvements in a process flow sheet, its power lies in its ability to analyze different process options and to pinpoint development needs. This is equivalent to the use of cycles in power plant design. We will present other examples later.

IV. Stoichiometric and Thermodynamic Constraints in Catalysis:

Choosing a set of reactions for modelling a complex system:

The SNG example above illustrated how catalyst properties impact process constraints and how global equilibrium constraints on methane yield are due to catalyst properties and are not a thermodynamic constraint. There is no thermodynamic reason why one could not develop a catalyst that promotes solely the reaction of converting to methane. Understanding how such constraints relate to catalyst properties is an important part of process design, and catalyst development. Thermodynamic analysis can help one understand the constraints that catalyst properties impose on complex reaction systems.

We begin with stoichiometry. Consider a set of reactions involving N species. Let the vector $\underline{n} = (n_j : j=1,2,\ldots,N)$ be the vector of moles of the N species. A set of reaction stoichiometrics between these species is [1,2,25,26]

$$\sum_{j=1}^{N} \nu_{ij} A_j = 0 \qquad (i=1,2,\ldots,S), \tag{10}$$

where ν_{ij} is the stoichiometric coefficient of the compound A_j in reaction i and S is the number of stoichiometric relations used to describe the reactions. If one starts with a given initial composition, vector $\underline{n}^o$, then one can express any composition resulting from this initial composition as

$$n_j = n_{jo} + \sum_{i=1}^{S} \nu_{ij} \xi_i , \tag{11}$$

where ξ_i is the extent of reaction i. We call the region of species space defined by the set of $\underline{n}$ satisfying both Eq. (11) and the condition $\underline{n} \leq \underline{0}$ the reaction hyperplane or the stoichiometric compatibility class associated with initial condition $\underline{n}^o$. In addition, let there be E element balances. To solely describe stoichiometry, global equilibrium and heat balances, one can arbitrarily choose any set of T independent stoichiometric relations, such that T=N-E. That is, the T vectors $\underline{\nu}^i = (\nu_{ij} : j=1,\ldots,N)$, i=1,2,...,T must be linearly independent. Finding such a set of reactions only requires knowledge of the number of possible compounds A_j. It is useful to realize that even knowledge of the set of possible compounds contains kinetic information since it is based on knowledge of which compounds are likely to form given the conditions and timescale of the reactor. Global equilibrium then is, in this sense, a kinetic concept dealing with a local (in the subspace of an even large composition space) minimum of free energy.

In choosing the set of species, one usually neglects free radicals and trace compounds since they usually only have negligible impact on stoichiometric computations. One also neglects species appearing only in the adsorbed phase on the catalyst surface despite the fact that they are present in large quantities. One implicitly assumes that one can treat a heterogeneous catalytic reaction as a pseudo-homogeneous reaction containing only the species participating in the homogeneous phase. One also generally assumes that such a pseudo-homogeneous reaction has the same thermodynamic stoichiometric constraints as the real reaction, including the law of detailed balancing. While this assumption is intuitively appealing, a proof only exists for first order reactions (49). Since the amount of adsorbed species in the reactor can easily be several times as large than that in reaction phase, such assumptions only make sense at steady state.

Although modelling a complex chemical reactor also employs Eq. (11), the choice of $\underline{\nu}$ underlying a suitable kinetic model is more complex, involving much more than simply a linearly independent set of reaction vectors. Simple knowledge only of the set of species is obviously insufficient. Clearly, the set of likely reactions must also play a role.

Now, what are "likely" reactions? Reactions used in modelling a chemical reactor do not describe real molecular events, but rather grossly represent many intermediate steps. Since intermediates are usually not directly accessible to experimental measurement, one would hope to model at least a steady system solely in terms of the concentrations of species appearing in the stoichiometric description. Furthermore, experiments observe concentration composition trajectories (rather than individual reaction rates) as functions of temperature, pressure, initial composition and space velocity. Given a stoichiometry one translates these trajectories into sets of reaction rates.

One way of choosing such a set of reaction rates for modelling is to try to observe the reactions under conditions where there are fewer possible compounds. Thus, to measure the importance of the reaction

$$C + 2H_2 \rightarrow CH_4$$

in the steam gasification of carbon, one can gasify carbon under conditions where no other compounds are formed. If one can model the total system based on such independently measured reaction rates, then the choice of $\underline{\nu}$ is obvious. In most cases this is not possible, and this is precisely when thermodynamics enters. It can yield a suitable ν solely from the set of observed compositions, without kinetic computations. First, plot the product composition, $\underline{n}$, of a plug flow reactor as a function of space velocity. This is a real trajectory since each point (i.e. composition) along the trajectory represents a composition in a particular cross-section along the plug flow reactor. The tangent of the trajectory is the direction of the vector $\sum_i \nu_{ij}\xi_i$ defined in Eq. (11). For a small increment in the length of the plug flow reactor, n_j is changed by the vector $\sum_i \Delta\xi_i \nu_{ij}$. By changing the initial conditions we can get a set of such trajectories.

The second law of thermodynamics requires that the free energy decrease along the trajectory (50). For an isothermal reactor this means that

$$\sum_{i=1}^{R} \Delta\xi_i \sum_{j=1}^{S} \nu_{ij}\mu_j \leq 0, \tag{12}$$

where μ_j is the chemical potential of species A_j and S are the number of reactions. We now impose an additional condition on the choice of ν_{ij} [24,50], i.e.,

$$\Delta\xi_i \sum_{j=1}^{N} \nu_{ij}\mu_j \leq 0, \qquad i=1,2,\ldots R, \tag{13}$$

Eq. (13) specifies that each reaction separately has to proceed in a direction of decreasing free energy. For this to be correct, the individual reactions making up the row of the matrix $\underline{\nu}$ must have some special properties. These reactions, each of which is really the sum of several steps involving intermediate compounds which do not appear in the stoichiometric description of the system in the fluid, must be able to proceed independently of one another; this is only possible if they have no joint intermediates. Eq. (13) is a way to express this independence quantitatively.

To model a reactor by a set of kinetic reactions, it is very important to use a set of overall reactions that has this property of kinetic independence. Dealing with molecular events would leave no flexibility in the choice of these reactions. However, if one deals with overall catalytic reactions, one can only make intelligent guesses, and then use Eq. 13 together with measured trajectories to test if a proposed set of such reactions is consistent with the data. Each reaction ν^i represents direction of a vector in composition space and a parallel one in the hyper plane of compositions described by (11). Let the positive direction of this vector be the direction indicating a decrease in free energy. Then (13) requires that thetangent at each point along every measured trajectory be a positive linear combination of these vectors. Ref. [50] does this in detail and provides examples. Fig. 8 illustrates this procedure in the context of a reaction system with 3 compounds, A,B,C, each having a free energy of formation of unity. At reaction temperature $\Delta G = 0$ for the reactions $A \rightleftarrows B$ and $A \rightleftarrows C$. The set of all possible reactions is assumed to be

$$A \rightleftarrows B,\ B \rightleftarrows C,\ A \rightleftarrows C. \tag{14}$$

Let APE be a hypothetical trajectory, and consider point P. The directions of the three kinetically independent individual reactions in composition space, $A \rightarrow B$, $B \rightarrow C$, $A \rightarrow C$ are parallel to the sides of the triangle. The direction of the vector corresponding to the reaction $A \rightleftarrows C$ is at point Pbetween those corresponding to the other two reactions. Thus, the vectors corresponding to the reaction A $\rightleftarrows$ B and B $\rightleftarrows$ C constrain the possible direction of the overall reaction vector at point P. As shown in Fig. 8, only trajectories whose tangents pass P between (i.e., are a linear combination with non-negative coefficients of) the vectors corresponding to reactions A -> B and B -> C can fulfill the requirement that free energy decreases for each individual reaction separately. Thus, we call the vectors corresponding to the reaction A -> B and B -> C <u>limiting vectors</u> at <u>point P</u>. All points inside the triangle AFE share the same limiting reaction vectors. The total mass balanced triangle ABC divides into six subsections, each having a different set of limiting reaction vectors. The lines dividing these sections are the equilibrium lines for the individual reactions; we call them "attractors." A trajectory that goes along an attractor in the global equilibrium direction is always permissible.

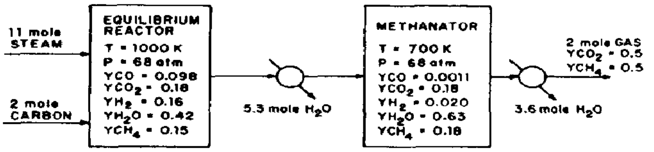


Figure 7 Conventional two-step process for production of methane

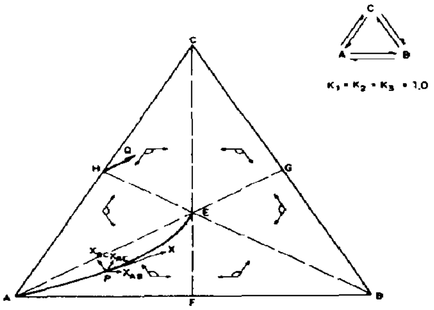


Figure 8 Thermodynamic limitations on kinetic trajectories for the isothermal monomolecular reaction system A,B,C
Each individual reaction separately fulfills the condition of decreasing free energy
APE - Hypothetical trajectory from pure A to equilibrium

In these three species examples where the stoichiometric compatibility class (cf., Eq. (11)) is two-dimensional, one can check the suitability of a given $\underline{\nu}$ for modelling the reactions by constructing a figure similar to Fig. 8 with the limiting vectors drawn in each subsection and the checking that no measured trajectory violates Eq. (13).

In a four species, three-dimensional stoichiometric compatability class, the equilibrium condition of each reaction forms a surface. These surfaces or attractors divide the space into regions in which the limiting vectors define a cone. The tangent of the trajectory must always lie "inside" the appropriate cone. Similar concepts apply to higher dimensions. However, in the three- or more -dimensional case, checking Eq. (13) inspection is difficult and one must apply (13) directly at each point along each measured trajectory.

Sets of $\underline{\nu}$ compatible with a given set of trajectories will not, in general, be unique. We say that any $\underline{\nu}$ that satisfires (13) for all measured trajectories is <u>sufficiently compatible</u>.

In addition, we try to find a $\underline{\nu}$ that corresponds to mechanisms havingT-N-E linearly independent reactions. We call such a set a <u>minimum set</u>. In general we begin by enumerating all possible minimum sets and then check for each whether it is also sufficiently compatible with all known trajectories. For example, in the three species case considered in Fig. 8, S-2, and the three minimum sets are:

I. A $\rightleftarrows$ B , A $\rightleftarrows$ C II. A $\rightleftarrows$ B , B $\rightleftarrows$ C III. A $\rightleftarrows$ C , C $\rightleftarrows$ B

For the trajectory APE in Fig. 8, both sets I and II are sufficient, whereas set III is not. Preferably, one should measure trajectories using different initial compositions.

It is certainly possible that no minimum set will be sufficient and that all three reactions may be required. In fact, a set comprised of all three monomolecular reactors may not even be sufficient; one might have to introduce additional overall reactions to achieve sufficiency. For example, the trajectory H-Q in Fig. 8 does not decompose into three monomolecular reactions. It follows the direction of the overall reaction

$$2A \dashrightarrow B + C \tag{15}$$

While (15) is stoichiometrically the same as the sum of reactions A $\rightleftarrows$ B and A $\rightleftarrows$ C, it is kinetically and thermodynamically different since it must involve different sets of intermediate compounds and steps. The fact that we need to introduce this reaction in addition to the individual reactions A -> B and A -> C to be able to decompose the trajectory consistent with Eq. (13) gives us an important information about the mechanism of the overall reactions occurring in the system. This is an example of thermodynamic coupling, a topic that we expound in section VIIa.

A Berty or stirred tank reactor [6,7,42] has some advantages in studying the kinetics of a complex reaction system. Varying the space velocity and plotting the composition with space velocity as the parametrization also yields a trajectory in composition space. However, in contrast to a plug flow reactor, such a trajectory is a purely geometric concept, since it does not represent any set of compositions actually inside a reactor. A single composition vector completely characterizes a steady state stirred tank reactor for a given space velocity and feed composition. This vector, $\sum_i \nu_{ij}\xi_i$, connects the initial composition to the product composition (see Fig. 9). It is much easier to accurately measure the direction of $\sum_i \nu_{ij}\xi_i$, and to apply condition (13) to it than to do the same for plug flow trajectory tangents (see Fig. 9). In both cases it is essential to use different feed compositions in order to obtain reliable information about permissible sets of $\underline{\nu}$

In many cases, the $\underline{\nu}$ and the corresponding reaction rates r_i $(\tau=1,2,\ldots,S)$ are little more than empirical fitting functions; one should ask what part of the information contained in it is crucial for building of a successful kinetic model. The value of $\underline{\nu}$ depends on the task of the investigator. A process designer, one who must fix the catalyst, the feed composition and the operating conditions differs from a reactor designer, one who chooses the reactor configuration and scales up a reactor for a given specific reaction, and given feed composition. While in the design of a reactor the choice of n^o and operating conditions are not completely fixed, the latitude of the latter in changing operating or feed conditions is rather narrow. Below we examine the answers appropriate to each.

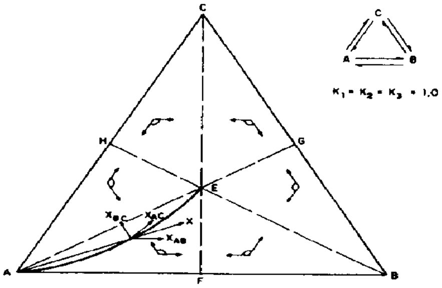


Figure 9 Thermodynamic limitations on kinetic trajectories in a stirred tank (Berty) reactor

Reaction system identical to Fig.6.

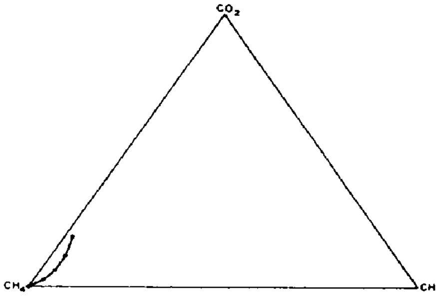


Figure 10 Selective Oxidation of methane to methanol

$CH_4 + \frac{1}{2} O_2 \dashrightarrow CH_3OH$

$CH_4 + 2\ O_2 \dashrightarrow CO_2 + 2\ H_2O$

Data from Ref.(15)

V. Minimum Information on the Reaction Kinetics required for Chemical Reactor Design

A critical aspect of any design problem is to understand what information is really essential for a successful design. Since information is often expensive or unavailable at the time of the design, the concept of minimum information is an essential part of any systematic design approach. One of the recurring problems in chemical reactor design and scaleup is the impact of mixing and transport processes on conversion and selectivity. A complete and reliable kinetic model is all the information one needs. This is seldom thecase at the time of design. In a complex system we frequently even lack reliable information about what reactions really occur. Here, the approach in Section IV can be very useful. Most of the essential information is contained in the trajectories, thus we look for a design approach that is directly based on the information contained in the trajectories.

We classify design problems into three types:

a) Totally constrained trajectory design
b) Focal point trajectory design
c) Minimax design.

a) Totally constrained trajectory design

Consider an ammonia reactor. The stoichiometric number of degrees of freedom is one. The possible reaction is a straight line in the stoichiometric compatibility class. All we need to know is the position of the equilibrium on this line and the reaction rate. Mixing and scaleup have no impact on selectivity, only on reaction rates and conversion. A similar case exists if T=2, but one reaction is fast. Consider for example the reactions in Fig. 8. If the reaction $B \rightleftarrows C$ is much faster than all other reactions, then all possible trajectories starting from A approach the line AE, which is the equilibrium line of the reaction $B \rightleftarrows C$. There is no way that one can learn what other reactions really occur from these trajectories. It could be $A \rightleftarrows B$, $A \rightleftarrows C$, or a more complex combination. But as long as one deals with scaleup in design, this is not essential. Mixing and scaleup will not impact selectivity, only rate. Optimal reactor design consideration and reactor choice therefore depend mainly on the form of an overall rate expression.

One can also provide a safety factor by over-designing the reactor. Strongly constrained trajectories can appear if T>2. They need not be straight lines, because individual reactions' equilibrium focuses in the stoichiometric compatibility class may be curved. (For an example, see the case of coal gasification discussed in Ref. 50). A methanol reactor with a copper chromium catalyst and a feed of CO, CO_2 and H_2 represents another example. Here, T=2 and the shift reaction is fast compared to the other reactions occurring. Others involve parallel reactions of equal order. One way to test how constrained the trajectory is, is to measure trajectories from different initial compositions in both a plug flow and a stirred tank reactor. Trajectories constrained to a particular curve will yield identical results in both reactors, and in strongly constrained trajectories the difference will be minimal over the whole trajectory.

b) Focal Point Trajectory Design

If the desired outlet composition is close to a global equilibrium all possible trajectories converge to it. We define such a design as a <u>focal point trajectory design</u>.

Focal point design problems share one feature with design problems for completely constrained trajectories. In all of these cases the exact form of $\underline{\nu}$ is not very important. If one knows the set of all species involved, all one needs to know is that there are a sufficient number of reactions to reach global equilibrium and what are their overall rates. Furthermore, one can protect oneself in scaleup by using a lower space velocity than the maximum required for the prescribed conversion. In other words, one can over-design the reactor to guarantee the conversion. The choice of the reactor that maximizes space velocity depends again on the reaction rate expression and on the form of the rate expression; these relations are well known.

c) Minimax Designs

A minimax trajectory refers to a design problem in which the desired product composition is far from global equilibrium and where one wants to maximize certain product concentrations, while minimizing others. An example is selective oxidation of ethylene to ethylene oxide, where one wants to maximize ethylene oxide, while minimizing CO_2 and H_2O formation.

Design problems involving minimax trajectories are the more challenging ones. Mixing and scaleup affect selectivity. It is harder to protect against yield losses and these losses have larger penalties. A detailed knowledge of $\underline{\nu}$, the overall reactions actually occurring, is useful and essential. There are two types of minimax trajectories:

A. Averageable trajectories
B. Non-averageable trajectories

We define these as follows: Assume one uses a plug flow reactor to measure a set of trajectories, each having a different feed composition. In addition, one has similar trajectories for a stirred tank reactor. In an averageable system, any outlet composition of a stirred tank reator can be written as a convex combination of plug flow compositions deriving from the same feed. For example, all first order reactions are averageable, since the outlet composition of a stirred tank is just the integral over the residence time distribution of plug flow product streams [51,54]. Many nonlinear and pseudo-linear reactions have the same property (see [54] and [64]). Examples are selective oxidation, hydrocracking, and simple consecutive reactions. One example, the selective oxidation of methane to methanol, is given in Fig. 10.

An example of a nonaverageable trajectory is

$$iC_4H_{10} + C_4H_8 \rightarrow iC_8H_{18}\ , \qquad (16) \qquad\qquad nC_4H_8 \rightarrow (C_4H_8)_n \qquad (17)$$

IF one feeds an equimolar ratio of reactants into a stirred tank operating at high conversion, it will have a higher iso-octane yield than is achievable in any plug flow reactor at any conversion deriving from the same feed (Fig. 11). This is due to the fact that reaction (16) is linear in butane concentration and reaction (17) is second order. A low concentration of butane suppresses reaction (17). In a stirred tank reactor the concentration is lower than the average concentration that obtains in a plug flow reactor with the same overall conversion. In a minimax design problem, it is very important to know if a reaction is averageable or not because this dictates one's choice of reactor configuration and the level of caution required for scaleup. Such knowledge is also helpful in designing experiments to determine the choice of a sufficient $\underline{\nu}$.

For any averageable reaction system, plug flow gives the best yields. This has been proved for first order reactions in both isothermal and externally temperature controlled non-isothermal systems [51]. While I know of no proof for the most general non-isothermal case, I find the validity of this conjecture almost intuitively obvious and I have never been able to find a counterexample. I find it a useful conjecture for design. For non-averagable trajectories, the situation is more complex. The optimum configuration may be neither plug flow nor a stirred tank, but rather a more complex multiple feed-point system. Alkylation serves as a good example. The alkylation reaction has undesirable side reactions such as

$$iC_8H_{16} + iC_4H_{10} \rightarrow C_{12}H_{26} \qquad (18)$$

A reactor configuration consisting of a plug flow reactor with a large excess of isobutane instead of a stirred tank minimizes these side reactions while maximizing isooctane. One achieves this excess by separating the isobutane from the product and recycling it.

Note that the amount and the quality of the information required about $\underline{\nu}$ and the rates are not the same for the four cases mentioned above. For the case of a strongly constrained trajectory with a single rate-controlling step and several reactions, it is impossible to determine $\underline{\nu}$ and r_i (i=1,...,.S) from the trajectories. Fortunately, in this case, this information is not necessary for reactor design.

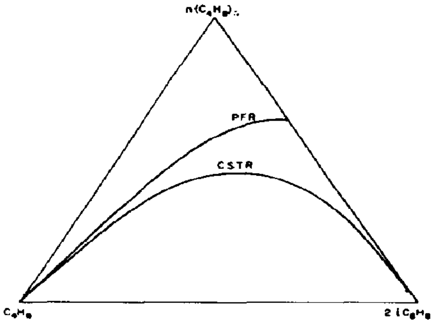


Figure 11 Kinetic trajectories of a nonaveragable reaction system

Alkylation of butane (reaction rates are hypothetical for illustration)

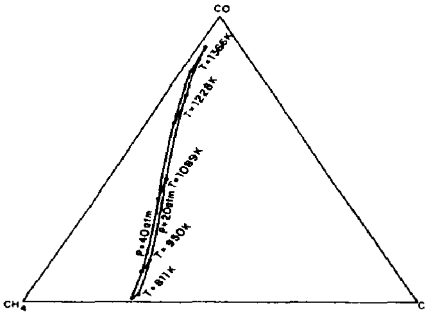


Figure 12 Equilibrium composition of the reaction system CH_4, O_2, H_2O, CO, H_2 and CO (Initial composition 1 mole CH_4 and 0.5 mole O_2, O_2 concentration at equilibrium is negligible)

For an averageable minimax trajectory, knowledge of $\underline{\nu}$ is much more useful since it allows one to direct attempts to improve the catalyst. But it is also not essential for reactor design because one can use the information contained in the trajectory in a direct way. For non-averageable minimax reactions a detailed understanding of $\underline{\nu}$ is essential for both reactor and process design. Thus, for the design of the alkylation reactor, one needs to understand the different reactions that might occur in order to choose a proper design.

For focal point design problems thermodynamics can also give the dependence of the equilibrium composition on temperature, pressure and feed composition. Since focal point designs are advantageous to minimax designs, one often tries to convert a minimax design into a focal point design. Two examples illustrate.

The production of syngas from methane by partial oxidation [33],

$$CH_4 + \frac{1}{2}O_2 \dashrightarrow CO + 2H_2 , \quad (19) \qquad CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O , \quad (20)$$

is a minimax problem since CO_2 and H_2O are formed as byproducts. However, if one runs the reaction at about 1000°C, the equilibrium composition consists mostly of CO and H_2 (Fig. 12), which gives the equilibrium composition (in terms of the carbon balance) as a function of temperature and pressure. The equilibrium concentration of O_2 is negligible. If one could find a catalyst which operated well at high temperatures, one would have transformed a minimax problem into a focal point problem. Indeed, several such catalysts are in the development stage.

A second example is methanol production by partial oxidation (Fig. 9), whose mechanism is

$$CH_4 + \frac{1}{2}O_2 \dashrightarrow CH_3OH, \qquad \Delta G^o_{298} = 27.7 \frac{kcal}{mole} , \qquad \Delta H^o_{298} = 30.2 \frac{kcal}{mole} ; \qquad (21)$$

$$CH_3OH + 1.5O_2 \dashrightarrow CO_2 + 2H_2O, \qquad \Delta G^o_{298} = -164 \frac{kcal}{mole} , \qquad \Delta H^o_{298} = -161 \frac{kcal}{mole} \qquad (22)$$

This is a minimax design problem (see Fig. 10) which, regrettably, cannot be transformed into a focal point problem because there is no equilibrium in which CH_3OH is maximized. One can, however, transform it into two focal point design problems carried out in separate reactors, by using the partial oxidation to syngas discussed in the previous example as a first step Low temperature conversion of syngas to methanol, which is again a focal point design problem, becomes the second step. This example illustrates an important use of thermodynamic analysis in process design. Thermodynamic analysis of possible reaction networks lends itself to searching for possible reaction pathways for new products [12,44,47,48,57,58,59].

VI. Thermodynamic Constraints on Accessible Composition Space

We ask: Given a specific catalyst that promotes a set of reactions $\underline{\nu}$ and r_i $(i=1,\ldots,R)$, what compositions can be reached (the set of accessible compositions) starting from given feed composition? If one could vary the rates of the individual reactions, what then would be the set of accessible compositions for a given $\underline{\nu}$?

There are two ways one can obtain such limits from a given $\underline{\nu}$. One is by modelling and varying the reaction rates of the individual reactions [21]. For first order reactions, Krambeck [35] has shown how this can be done in a simple, rigorous way. For many averageable reaction systems, one can probably use his method to get approximate results even if the reactions are not first order. Another option is to use the methods based on limiting vectors outlined elsewhere [50]. This is illustrated in Fig. 13 where we give the set of accessible compositions for the system, $A \rightleftarrows B$, $A \rightleftarrows C$, $B \rightleftarrows C$.

As discussed in section IV, Figs. 8 and 9 at each composition in the stoichiometric compatibility class ABC, all possible directions of the trajectory are constrained by two limiting vectors. In a higher dimensional case the limiting vectors would form a cone. We also showed that the equilibrium lines of the individual reactions divide the plane into regions in each of which the directions of these limiting vectors are uniform. At the equilibrium lines the direction of the limiting vector, the reaction which determines the limits on a trajectory, may change. If one starts at any initial composition one can then map out a region by continuing along a limiting vector until one hits the boundary or a single reaction equilibrium line, whichever comes first. Each time one hits a local equilibrium line, one follows the limiting vector which is closest to the stoichiometric boundaries of the composition plane. In Fig. 13 we illustrate the procedure for the case given in Eq. 8, using pure A as the starting composition. The accessible region starting from A is AHIJFA. In this procedure the thermodynamic constraints determine the permissible direction of reaction vectors at each composition. However, they do not determine their relative magnitudes.

We use the concept of the set of accessible compositions differently from Krambeck, who fixed the ratio between reaction rate constants. We allow this ratio to vary in the stoichiometric compatibility class. The result is a set of compositions reachable not by a single catalyst, but by a sequence of catalysts promoting only the set of reactions assumed. While the entire set of compositions computed this way may not be accessible in practice, all accessible compositions are contained within it.

In a stirred tank reactor, the set of accessible compositions differs from that in a plug flow reactor because instead of being described by a trajectory, a stirred tank is described by a single vector from the initial composition to the final composition. Moreover, this vector must be a positive linear combination of the limiting vectors in the corresponding region of this composition plot. In the example discussed, the accessible space for a stirred tank reduces to the trapezoid AHEFA.

Let us consider the role of the catalyst in determining the set of accessible compositions. Until now, we have assumed that all three reactions occur. If our catalyst did not promote one of the reactions, this fact would affect the set of accessible compositions dramatically. For example (see Fig. 14), if, for catalyst X, reaction $A \rightleftarrows C$ is slow compared to the other two reactions, the set of compositions accessible from a feed consisting of pure A is the region AEFA. If, on the other hand, one has another catalyst, Y, which does not promote the reaction $B \rightleftarrows C$, the set of composition accessible from a feed consisting of pure A is AHIEJFA, which is only slightly smaller than the region reachable using all three reactions. For this feed, catalyst Y is preferable to X in order to fulfill specs that prescribe a composition not reachable by X.

One can analyze much more complex reaction systems in a similar way [50]. This procedure allows one to estimate the limits on the potential value of new catalysts that promote an additional, more desirable reaction path in a complex system. It also permits fast screening of new catalysts. One can detect if a new catalyst promotes a reaction different from available catalysts if one measured composition is outside the accessible space of available catalysts. A practical example will be given in the next section.

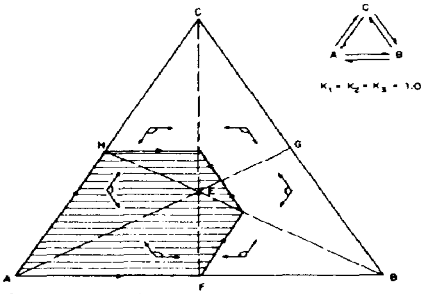


Figure 13 Accessible composition space (shaded area)
Reachable from point A, with 3 monomolecular reaction

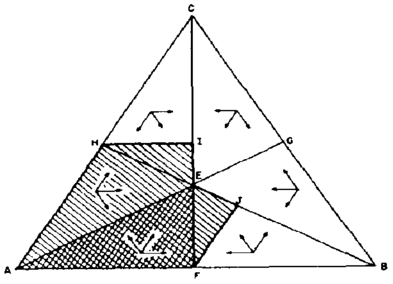
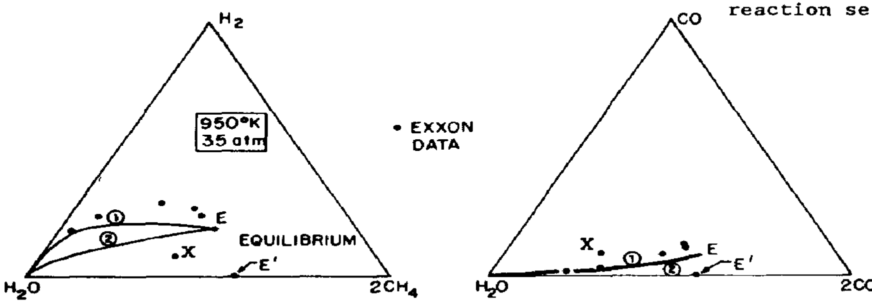


Figure 14 Area AEFA - Accessible composition starting with pure A realized by the reaction set A <—> B, B <—> C
Area AHIEJF - Accessible composition space starting with pure A realized by the reaction set A <—> B, A <—> C



① $C + H_2O \rightleftharpoons CO + H_2$ SLOW
$CO + H_2O \rightleftharpoons CO_2 + H_2$ } IN EQUILIBRIUM
$3H_2 + CO \rightleftharpoons CH_4 + H_2O$ }

② $C + H_2O \rightleftharpoons CO + H_2$ SLOW
$CO + H_2O \rightleftharpoons CO_2 + H_2$ } IN EQUILIBRIUM
$C + 2H_2 \rightleftharpoons CH_4$ }

Figure 15 Kinetic trajectories of catalytic (K_2CO_3) steam gasification of char (data from Exxon 1978)
E' - Equilibrium point for reaction 1 only
X - Composition obtained over a hypothetical new catalyst requires reaction set E or F (table 1)

VIa. Application of Thermodynamic Constraints to the Screening of Catalysts

The example involving methane given in Section III also illustrates how the above principles can screen new catalysts. Earlier we showed how to set up a kinetic model for a process involving several reactions. Table 1 gives several possible choices for $\underline{\nu}$, for methane formation from carbon and water. Case A contains all the reactions that are known to occur in this process. Cases B, C and D contain only minimum sets based on the reactions in Case A. Cases E and F contain minimum sets that have at least one alternative pathway giving direct methane formation. Each of the individual reactions is really a complex set of reactions involving intermediates. However, none of these intermediates appears in large quantities in the gas phase. Thus, one can write them as overall reactions.

Fig. 15 gives some experimental results from Ref. [20] for a reaction catalyzed by potassium carbonate. One can now test each set $\underline{\nu}$ by the criterion that the tangent at each point along the trajectory can be written as a positive linear combination of the limiting vectors corresponding to the $\underline{\nu}$ chosen. This can be done for sets A,B,C,D. Since B,C, and D are minimum sets, the decompositions of the tangents are unique. Since B,C, and D are sufficient, minimum sets, A is also satisfactory though its decompositions are non-unique. Minimum sets are desirable, since they allow faster screening.

Sets A,B,C and D all give maximum yields of methane at equilibrium. This results in a focal point reactor design problem. For process development of such problems the distinction between the different minimum sets is not essential. If one wants to maximize direct methane yield, one has two choices: either develop a low temperature catalyst with a more favorable equilibrium, (see Section 3 and Fig. 2), or find a catalyst in which methane yield is not constrained by equilibrium. A catalyst that promotes the reactions in sets E and F would have this property. The above method gives here a simple test for screening such a catalyst. All one would have to find is a single composition not accessible by the reaction set A and accessible in the way defined here by the set E or F. An example would be composition X in Fig. 15, which is reachable by sets E and F, but by none of the others. In screening new catalysts it is not important initially whether the catalyst leads to economically attractive results. What is important is to reliably recognize new chemical pathways. Our method could be a powerful tool for many other complex systems where one must look for catalysts for novel chemistry.

VII. How to Overcome Constraints Imposed by Catalyst Properties

In methane production the low methane yield at global equilibrium was an example of a catalytic constraint imposed by catalyst properties. It is not a consequence of the second law but a second law implication of the properties of a catalyst. It is important to understand this difference and the underlying reasons for the constraints. Real second law constraints give absolute limits. Second law implications sometimes can be overcome if one understands the reasons leading to them. Here, thermodynamics can provide a powerful tool for process improvements.

There are several options that one can use to overcome constraints resulting from catalyst properties.

1) Search for catalysts with different properties
2) Use two or multiple step nonisothermal reactors, which are often accompanied by an increase in number of chemical species involved.
3) Use selective separation processes, i.e., look for the equivalent of a semipermeable membrane.

VIIa. Changing Catalyst Properties: The Concept of Coupling

In the methane example (V) we began discussing how a new catalyst can change the set of reachable compositions. Fig. 16 gives the diagram of this monomolecular example with the set of reachable compositions for the three monomolecular reactions. In addition, the figure also presents two other limiting curves. One is the composition space obtainable in an isothermal reactor, if one only requires the free energy of the products to be less than or equal to that of the feed. In the case where the free energies of formation of all three compounds are equal this condition is vacuous and the entire triangle is accessible. However, there is no way to reach the entire triangle in a conventional reactor; it requires semipermeable membranes (see Fig. 1): one that is only permeable to A and admits A into the system, and a second that selectively removes either B or C. Inside the membrane one can use any catalyst that drives the reaction towards equilibrium. A reactor system equipped with such hypothetical membranes would effectively allow one to go from pure A to pure B, whereas a conventional reactor would be limited by the equilibrium between A and B. In the absence of such a membrane one is faced with a thermodynamic constraint that is imposed by using any catalytic reactor that has mixed product removal, i.e., that free energy must decrease monotonically along any possible trajectory. Fig. 16 shows the isoclines of free energy and also shows the impact of this additional constraint on the set of reachable compositions. The boundary of this region is much more generous than the one in Fig. 14, which contains the set of reachable compositions for the reaction $A \rightleftarrows B$, $B \rightleftarrows C$, $A \rightleftarrows C$. To achieve a composition close to the boundary of the region determined by the free energy constraint, one must find a catalyst that promotes more complex reactions than this monomolecular set. Fig. 17 illustrates the impact on the set of reachable compositions of the addition of a more complex reaction to the scheme, and, in particular, of the addition of $2A \rightleftarrows B + C$ to the three reactions in Fig. 13. The accessible region is significantly larger than that determined by the three monomolecular reactions alone. Consider Fig. 17, point H, where the reaction $A \rightleftarrows C$ is at equilibrium. A reaction trajectory starting from composition H in the direction H-Q has a decreasing free energy and should therefore be permissible. But the three reactions in Fig. 13 do not, by themselves, admit such a trajectory because along this trajectory reaction $A \rightleftarrows C$ increases free energy, even though reaction $A \rightleftarrows B$ decreases it.

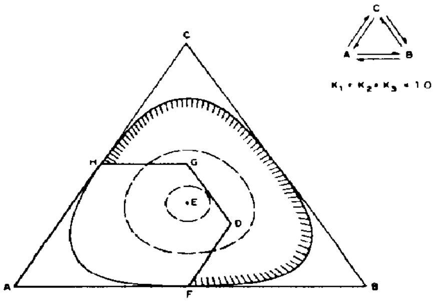


Figure 16 Accessible composition space from point A for ΔG<0, between initial and final conditions, all compositions in triangle
Area AHCDFA for reaction A <—> B, B <—> C, A <—> C
ᴛᴛᴛᴛᴛᴛ Accessible composition space of trajectories for ΔG ≥ 0

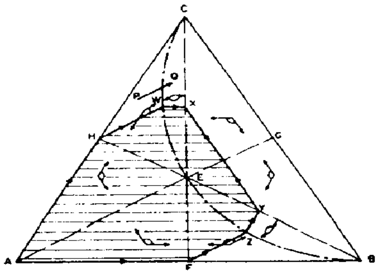


Figure 17 Same as Figure 4, but the reaction 2A <—> B + C has been added to the reaction set of Eq.(2)

If A -> B and B -> C are kinetically independent chemical reactions, there is no way that they can transfer free energy to each other in an isothermal reactor. The reaction $2A \rightleftarrows B + C$ is the stoichiometric sum of these two monomolecular reactions, but it must be an overall independent reaction in its own right. That is, it must have a disjoint mechanism, i.e., a set of intermediates disjoint from those of the two individual monomolecular reactions. An example would be

$$2A \leftrightarrows M \leftrightarrows B + C \ , \qquad (23) \qquad\qquad 2A \rightleftarrows B + C \ , \qquad (24)$$

The intermediate M couples the two reactions stoichiometrically. If the concentration of M is negligible, the observable reaction resulting from reaction (23) can be written as
If (24) occurs it must be added to the three kinetic independent reactions, which describe the system, since it creates new permissible trajectories.

We define an overall reaction that can be broken down into two simpler reactions as a coupling reaction if it permits trajectories which are thermodynamically not permitted by the two separate simpler reactions. If M only occurs in the adsorbed phase (or in very small concentrations in the fluid phase), it does not affect the overall free energy constraints of the trajectory. We would normally not include it in the description of the steady state reactor. But, this intermediate permits a direction which was not permitted by the three monomolecular reactions. In Ref. (50) we called this effect "the coupling of two reactions." Actually, there is no way that one can really couple to overall chemical reactions. All one does is find suitable intermediates to achieve overall reactions having the desired trajectory and overall effect. However, it is useful to introduce the concept of coupling for the process designer, who normally defines goals in terms of stoichiometry. Thus, if one wants to achieve an organic synthesis involving an increase in free energy to be supplied by combustion, one defines the main reaction as the goal and considers the combustion a tool to supply the free energy for that goal. However, if reaction mechanisms which achieve the same overall goal without any heat transfer exist, they have significant advantages. Thus, "coupling" is a process design concept which is useful for catalyst characterization and development.

Nature is forced to play this game all the time because all biological reactions are isothermal. It therefore lacks one principal trick for carrying out reactions with positive ΔG, i.e., to raise the temperature until ΔG becomes small or negative and until the free energy of the heat of the reaction can generate the increase in free energy. Biological processes operate close to the temperature of the environment, and the free energy of the reaction heat is close to zero. Therefore, nature must rely on separation processes and on coupling. The Krebs cycle is an example of such coupling. One net reaction in the cycle is the combustion of glucose to CO_2 and water. The other net reaction is transformation of ADP to ATP, which has a positive ΔG. It is achieved by a complex reaction mechanism in which each reaction has a decreasing free energy. The net result is a coupling of the two overall stoichiometric relations. The increase of free energy in this reaction allows, by its reversal, the isothermal conversion of chemical energy to mechanical energy. The only other way that nature can increase free energy of a compound is by photosynthesis.

I have found it hard thus far to identify examples of such coupling in practical catalysis, although they probably exist. Such examples are worth looking for. I give only one example of current interest in catalyst and process research, namely, oxidation coupling of methane conversion [36].

The standard way to convert methane to liquid fuels has the overall reaction

$$CH_4 + \frac{1}{2}O_2 \dashrightarrow \frac{1}{n}(CH_2) + H_2O. \qquad (25)$$

An example might be

$$CH_4 + \frac{1}{2}O_2 \dashrightarrow \frac{1}{2}C_2H_4 + H_2O \;; \qquad \Delta G^o_{298} = -34.4\ \frac{kcal}{mole}\ , \quad \Delta H^o_{298} = -33.7\ \frac{kcal}{mole} \qquad (26)$$

It is normally done in multiple steps where CH_4 is first converted to syngas and then either directly to hydrocarbons by Fisher Tropsch liquids or first to methanol and then to hydrocarbons. Another more desirable overall reaction would be

$$CH_4 \dashrightarrow \frac{1}{2}C_2H_4 + H_2 \;; \qquad \Delta G^o_{298} = 23.3\ \frac{kcal}{mole}\ , \qquad \Delta H^o_{298} = 24.1\ \frac{kcal}{mole} \qquad (27)$$

The ΔG is positive. One cannot achieve acceptable conversion at reasonable temperatures. If one could couple reaction (27) with (26), one would get the reaction

$$2CH_4 + \frac{1}{2}O_2 \dashrightarrow C_2H_4 + H_2O + H_2 \;; \qquad \Delta G^o_{298} = 14.4\ \frac{kcal}{mole}\ , \qquad \Delta H^o_{298} = -9.6\ \frac{kcal}{mole} \qquad (28)$$

Such a process would be very desirable. If a process could realize Eq. (28), it could revolutionize the conversion of methane to liquid products.

Regrettably, the amount of oxygen consumed by a practical catalyst system for oxidative coupling is more than 0.5 mole per mole methane. The reason is that H_2 and other products react faster with O_2 than CH_4. This does not rule out the existence of a coupling reaction such as (28). One possible way for this coupling to occur is

$$\begin{aligned}
&2CH_4 \rightarrow 2CH_3{*} + 2H{*}\\
&2H_2{*} + M_eO_2 \rightarrow H_2 + M_eO\\
&2CH_3 \rightarrow C_2H_6 \qquad\qquad\qquad\qquad (29)\\
&C_2H_6 \rightarrow C_2H_4 + H_2\\
&M_eO + \frac{1}{2}O_2 \rightarrow M_eO_2 .
\end{aligned}$$

In (29) ethane is an intermediate which, at sufficiently high temperatures, could decompose to C_2H_4 and H_2. Other intermediates are also possible.

To understand the impact of the coupling, let us look at this example (Fig. 18) in analogy to Fig. 16. We plot an equivalent design for the reaction system made up of the compounds CH_4, O_2, C_2H_4, H_2O and H_2, where $N=5$, $E=3$ and there are two degrees of freedom. Each two-dimensional plot corresponds to a different value of

$$CH_4 + H_2 + H_2O = \text{constant}, \qquad (30)$$

which is just the difference of the element balances for oxygen and for hydrogen.

The feed is 1 mole CH_4 at .25 moles oxygen, 1 atm pressure and 1000°C, which gives the accessible region ABFBA. In terms of the conditions of decreasing from energy, all compositions along the line DF can be approached arbitrarily closely. Consider first the reactions parallel to the sides of the triangle:

$$2CH_4 + O_2 \rightleftarrows C_2H_4 + 2H_2O \qquad (31) \qquad\qquad 2CH_4 + \rightleftarrows C_2H_4 + 2H_2 \qquad (32)$$

$$2H_2 + O_2 \rightleftarrows 2H_2O \qquad (33)$$

For reactions (31) and (33), the local equilibrium line is the line DF. This is due to the fact that in both reactions the equilibrium contains very little oxygen and, for practical purposes, one can neglect oxygen when plotting the stoichiometry of equilibrium compositions. The local equilibrium line for reaction (32) is line GE. If all the reactions are possible, the set of accessible compositions is ADJGA. The same is true for the minimum set (31),(32). However, for the minimum set (31),(33), the set of accessible compositions reduces to ADEGA. Introduction of reaction (28) increases the set of accessible compositions to ADFHGA, which is a significant improvement.

One can couple Eqs. (31) and (32) in different ways by varying the coefficients in (27). We have no idea if such overall reactions will ever be achieved, but this procedure illustrates the potential process advantage of finding catalysts with a suitable reaction mechanism.

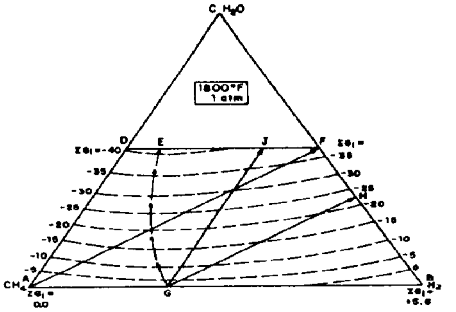


Figure 18 Oxidative coupling of mwthane

AF : $2CH_4 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O + H_2$ (28)

AD : $2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$ (31)

AG : $2CH_4 \rightarrow C_2H_4 + 2H_2$ (32)

BF : $2H_2 + O_2 \rightarrow 2H_2O$ (33)

Accessible composition spaces
Reaction 31, 32, 33 (ADJGA)
Reaction 28, 31, 32 (ADFHGA)

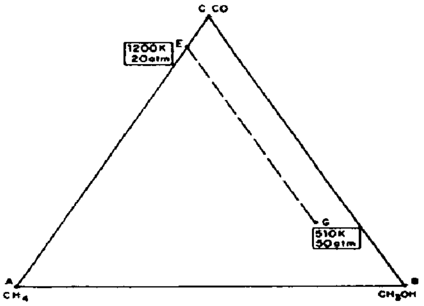


Figure 19 Two step process for methanol

Equilibrium system of CH_4, H_2O, CH_3OH H_2, CO from initial 1 mole CH_4 2 mole H_2O

Global equilibrium close to line AC

First step global equilibrium at 1200 K, 20 atm, point E

Second step equilibrium of reaction $CO + 2H_2 \rightarrow CH_3OH$ at 510 K, 50 atm(G)

VIIb. Two-Step Nonisothermal Processes

One normally applies this method when the conversion to the desired product is limited by the equilibrium in a isothermal reactor. The first isothermal reactor converts the feed to intermediates. The second, under different operating conditions with the proper catalyst, can further react these intermediates to the desirable product.

This technique uses the thermodynamic constraint of equilibrium in order to achieve higher overall conversion of the feed despite the absence of a single favorable catalyst. It is also useful when there is no isothermal pathway to the desired product. In most cases one of the reactors runs an exothermic reaction and the other an endothermic one. This method is very widely used in reactor design. It is important to understand the reasons for it and the thermodynamic considerations involved in executing it.

Consider, for example, the reaction system

$$CH_4 + H_2O_{(g)} \rightarrow CO + 3H_2 \;;\quad \Delta G^o_{298} = 34.0\ \frac{kcal}{mole},\quad \Delta H^o_{298} = 49.3\ \frac{kcal}{mole} \qquad (34)$$

$$CO + 3H_2 \rightarrow CH_3OH + H_2 \;;\quad \Delta H^o_{298} = 21.7\ \frac{kcal}{mole}\quad \Delta G^o_{298} = -6.0\ \frac{kcal}{mole} \qquad (35)$$

The net reaction is

$$CH_4 + H_2O \rightarrow CH_3OH + H_2;\quad \Delta G^o_{298} = 28\ \frac{kcal}{mole}\quad \Delta H^o_{298} = 27.6\ \frac{kcal}{mole} \qquad (36)$$

In reaction (36), ΔG is large and positive and the difference between ΔG and ΔH is very small. The overall reaction has very low conversion at all reasonable temperatures. Furthermore, at sufficiently high temperature methanol is unstable. Addition of CO and H_2 to the set of species still does not allow any reasonable conversion to CH_3OH in an isothermal reactor. If the reaction scheme included consecutive reactions first forming CO and H_2, then the maximum yield of CH_4 would be the equilibrium amount. Fig. 19 gives the equilibrium compositions; they lie practically on the CH_4 -> line. An alternate design would first convert to CO and H_2 at a high temperature (point AE in Fig. 19), and then proceed at lower temperature to methanol, (line EG in Fig. 19). This is the main reason for carrying out a nonisothermal two-step process. There is a significant literature on optimizing temperature profiles in reactors, but, in practice, nonisothermal reactors are mainly used to overcome thermodynamic constraints.

In most of the cases the nonisothermal route also involves introduction of new species and enlargement of the stoichiometric degrees of freedom. In the case of methanol from methane (reaction (36)) the introduction of additional species into the overall reaction mechanism was essential in order to achieve a useful trajectory. In the case of methane from coal (section III), the additional compounds (H_2,CO) came directly from the reaction mechanism. Its two-step process was not required by overall thermodynamic constraints as in Eq. (36), but it was rather a result of the lack of a suitable catalyst. It is important to distinguish between these two cases, even when the final designs are similar, because one can change one of these to a one-step design by finding a suitable catalyst, whereas one cannot do the same for the other (Eq. 36). A case similar to Eq. (36) is the production of hydrogen from coal, where a two-step process is dictated by the thermodynamic constraint of the overall process.

VIIc. How to Imitate a Semipermeable Membrane

A) Integrate a separation process into the reactor.

If, for some reason, one cannot run a reactor such that ΔG is reasonably negative, one must generate free energy by a separation process. An exception is a process with a large contraction of volume where the compression of the feed creates free energy.

The problem with generating ΔG by separation is that separations are very often highly inefficient and costly. For example, the cryogenic separation in Fig. 6 has an efficiency of less than 10%. This is one area where thermodynamic analysis shows that the potential for improvement is tremendous. For the reaction and process engineer this information is not useful in the context of a specific process because these inefficiencies are inherent in present separation technology and apply to all processes.

Even when separations are easy (such as in a methanol reactor; see Fig. 20), they are energy inefficient. The scheme in Fig. 20 imitates a semipermeable membrane (methanol is removed from the recycle), but it has two energy penalties which are not related to the thermodynamic constraint. First, one must exchange heat to preheat the recycle. The driving forces required impose a significant heat loss. Second, there is a large pressure drop related to the recycle.

Attempts have been made to reduce losses due to cooling, heating and compressing recycle streams. For example, Westerterp has developed an interesting scheme for methanol production in which a solid adsorbent is fed with the gas. This allows high once-through conversion, but requires recovery of the methanol from the adsorbent [66]. Kadlec [63] has suggested achieving the same goal by incorporating the adsorbent into the packed bed reactor and operating the reactor in a periodic manner. Chem Systems has tried to develop a slurry reactor in which the liquid is a solvent for methanol. The solvent can be recycled through a methanol desorber, which acts as a selective high temperature separation process. No suitable solvent has been found but the idea is intriguing and in the right direction. Another example is a catalytic process for MTBE where the reaction is carried out inside a distillation column. Considerable research is going on to integrate membranes directly into a reactor, although most membranes are very slow and expensive, limiting the application at present to high value products [43].

Another interesting realization of the membrane idea is the use of metal oxides or of other oxygen donors as transfer agents for oxidation. In butane oxidation to maleic anhydride, as in many other oxidation processes, one is faced with the dilemma of using either air or pure oxygen as the oxidizing media. If oxygen is used, it must be separated from air at a practical separation efficiency of less than 5%; if air is used, one must separate the product from the air.

Recently, DuPont [14] has demonstrated another option, which is shown in Fig. 21. A vanadium phosphate catalyst with a circulating catalyst oxygen donor oxidizes butane to maleic anhydride in the oxidation reactor by donating oxygen. The catalyst is then reoxidized with air in a separate zone. Neither the air nor the oxygen is in direct contact with the butane. The circulating catalyst acts as an oxygen carrier.

This process is equivalent to a semipermeable membrane, which separates the oxygen from the air and transfers it to the maleic anhydride reaction. Such a separation is, in practice, far cheaper both in capital and in energy costs, than separating oxygen from air.

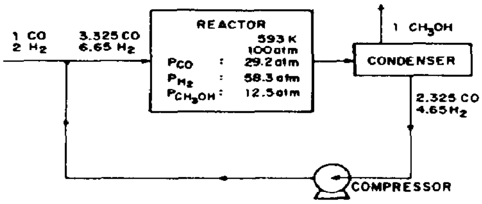


Figure 20 Reaction system for converting syngas to methanol

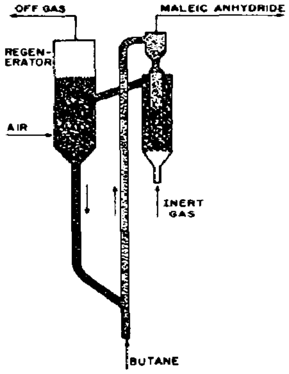


Figure 21 Schematic of recirculation solids reactor for production of maleic anhydride by partial oxidation of butane Ref. (14)

VIII. Shape Selective Catalysts

A partially selective semipermeable membrane is really a diffusion process with strongly differing diffusion coefficients. Most such membranes are expensive and comparatively slow. But one recent development in catalysis that revolutionized zeolite catalysts is based on the same idea. Shape selective zeolites are zeolites in which the crystal structure has channels whose cross-sections are similar in size to that of certain reactants. Only molecules below a certain size can access the active sites in these channels (or micropores). For example, in HZSM5, the diffusion of paraxylene in the pores is an order of magnitude faster than that of orthoxylene or methaxylene [13,65]. If one carries out a reaction such as toluene disproportionation

$$C_7H_8 \; {-}{-}{>} \; C_6H_6 + C_8H_{10}(O,\gamma,m) \qquad (37)$$

in such a shape selective catalyst, the paraxylene will escape the crystal channels faster than the orthoxylene and the metaxylene. Since the catalyst also promotes isomerization of the xylene, the net reaction is a preferential formation of paraxylene. In contrast, standard catalysts form an equilibrium xylene mixture. Here again, the reactor contains its own separation process: selective diffusion.

Such a catalyst is different from the semipermeable membranes mentioned above (Fig. 1). The present system, unlike the system in Fig. 1, must still satisfy $\Delta G \geq 0$ along any continuous phase trajectory. However, it can overcome the equilibrium constraint for consecutive reactions. Consider, for example, the reaction

$$A \rightleftarrows B \rightleftarrows C$$

in which C is the desired product (see Fig. 22). Suppose the equilibrium composition contain very little C. Even though the reaction $A \rightleftarrows C$ has good equilibrium conversion, this fact is not helpful unless a catalyst which promotes the direct reaction $A \rightleftarrows C$ and suppresses the reaction $A \rightleftarrows B$ is available. If such a catalyst does not exist, but a shape selective catalyst in which the reaction B $\rightleftarrows$ C is fast and A and C have much higher diffusion rates than B does exist, equilibrium between B and C will be established in the pore, but C will preferentially diffuse out. This is conceptually similar to the scheme in Fig. 23 in which the catalyst is separated from the fluid by a semipermeable membrane that only allows A and C to pass. Species B builds up to a concentration in equilibrium with that of A on the outside, and C escapes continuously. The catalyst behaves exactly like a catalyst having a site that preferentially promotes the reaction A $\rightleftarrows$ C. The tremendous value of shape selective catalysts is that they integrate selective transport process with catalysis in a way which is not only energy efficient, but also relatively cheap. Since selective transport processes and selective membranes impact reactors in similar ways, they can be considered practical realizations of the membrane concept. In this way the catalytic chemist imitates nature, which also surrounds many of its enzymes with selective membranes [43].

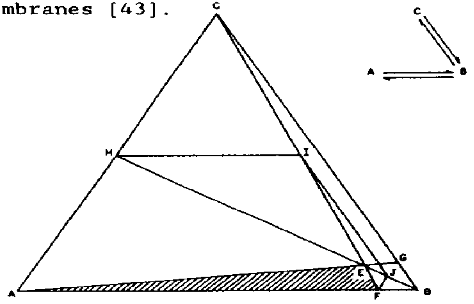


Figure 22 Monomolecular reaction system (A,B,C) with K_{AB}=10, K_{BC}=0.1

Area AFE: Composition space accessible by regular catalyst

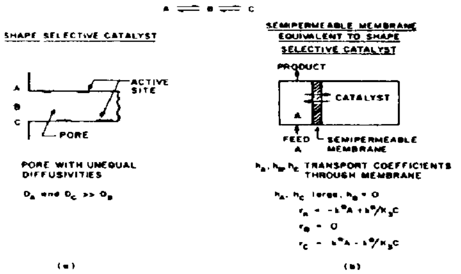


Figure 23 a) Simplified model for shape selective catalyst

b) An equivalent semipermeable membrane model for a shape selective catalyst

IX. Research Problems to be Solved

In the preceding I tried through examples to show how to combine thermodynamic analysis with a knowledge of kinetics to provide a powerful analytical tool for chemical reactor design and for chemical process design. The key is to understand that thermodynamic constraints met by a design are not always due to the second law itself, but are often consequences of other constraints, such as the lack of suitable materials of construction or the lack of a proper catalyst. If one understands the natures of the real constraints, one can often circumvent them. In this sense, thermodynamic analysis can be a powerful tool to suggest directions for process and catalyst development.

Such thinking should be a major step in any early stages of process development and should be helpful in the search for new routes to desired compounds. However, even though we have made considerable progress in this direction, there are still many interesting problems to be solved. A few important ones are:

...The use of the methods outlined above for the study of the mechanisms of catalytic reactions.

...The role of selective transport processes in catalytic media.

...The use of unsteady processes and the role of oscillations in modifying thermodynamic constraints imposed by catalyst properties.

Recently, I have been especially intrigued by this last problem because nature not only uses coupling and selective transport processes, but also carries out many reactions in an oscillatory mode. Section IC pointed out that a description of the reactions in a heterogeneous catalyst system, based solely on the concentration of species present in the fluid phase, probably only makes sense for steady state systems. How these constraints then apply to the unsteady reactor is a fascinating question. Understanding it may give some clues as to how thermodynamic constraints imposed by catalyst properties could be overcome by operating a reactor in an unsteady or oscillatory mode. This is both a challenging and a practical research problem since even forcing a reactor to oscillate can affect selectivity [11,22].

Table 1. Alternative Sets of Reactions for Steam Gasification of Carbon

$CO + H_2O \rightleftarrows CO_2 + H_2$ $CO + 3H_2 \rightleftarrows CH_4 + H_2O$ $C + 2H_2 \rightleftarrows CH_4$ $C + CO_2 \rightleftarrows 2CO$ Set A	$C + H_2O \rightleftarrows CO + H_2$ $CO + H_2O \rightleftarrows CO_2 + H_2$ $CO + 3H_2 \rightleftarrows CH_4 + H_2O$ Set B	$C + H_2O \rightleftarrows CO + H_2$ $CO + H_2O \rightleftarrows CO_2 + H_2$ $C + 2H_2 \rightleftarrows CH_4$ Set C
$2C + 2H_2O \rightleftarrows CH_4 + CO_2$ $CO + H_2O \rightleftarrows CO_2 + H_2$ $CO + 3H_2 \rightleftarrows CH_4 + H_2O$ Set D	$3C + 2H_2O \rightleftarrows CH_4 + 2CO$ $CH_4 + H_2O \rightleftarrows CO + 3H_2$ $CO + H_2O \rightleftarrows CO_2 + H_2$ Set E	$2C + 2H_2O \rightleftarrows CH_4 + CO_2$ $CO + H_2O \rightleftarrows CO_2 + H_2$ $CO + 3H_2 \rightleftarrows CH_4 + H_2O$ Set F

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