An Attainable Region Approach to Chemical Reaction Equilibrium

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Abstract

Consider a process with a defined feed(s) and a set of potential products. The Material Balance Limited Attainable Region (ARMB) encompasses all feasible combinations of process product streams consistent with the feed(s). The dimension of the ARMB is equal to the number of independent material balances (IMBs) that define the relationship between the process species. We can transform ARMB into a 2D region in the space of Gibbs Free Energy (G) and Enthalpy (H), designated as the Thermodynamic Limited Attainable Region (ART). At a temperature of To=25°C and ambient pressure, the ART(T0) represents the required process work and heat flows needed to transform a given feed into a specified product. However, the ART(T) describes the driving forces governing chemical transformations within reactors under different temperatures T. In particular, the minimum G on the boundary of the ART(T) is related to thermodynamic equilibrium. We describe how the ART is a simple but powerful representation of all possible reactions consistent with the given atomic inputs and how it can facilitate the identification of shifts in equilibrium species with temperature and assess the anticipated sensitivity of process outcomes to varying conditions. We demonstrate this conceptual framework across diverse processes, encompassing biological and emerging eco-friendly feeds.

**Keywords**: Material Balance Limited Attainable Region, Thermodynamic Attainable Region, Reaction Equilibrium.

* 1. Introduction

The early research by Shinnar (1998) demonstrated how thermodynamic constraints can be leveraged to design chemical reactors and improve thermal efficiency. He asserted that the limitations on efficiency are imposed by technology and catalysts rather than thermodynamics. Shinnar defined the reachable or accessible 'composition space' for a reacting system, bounded by overall specified reactions, where ΔG ≤ 0. He computed reachable compositions for systems with multiple reactions demarcated by iso-G lines. This approach considered both individual and combinations of reactions, offering insights into potential reaction routes to overcome thermodynamic limitations and facilitate the development of novel catalysts. However, this visualization is constrained by the dimensionality of the problem, limited by the number of species involved.

Understanding thermodynamic constraints, namely enthalpy (H) and Gibbs Free energy (G), is crucial for designing more efficient chemical and biochemical processes that meet emission targets. Efficient utilization of raw materials and optimized heat and workflows are critical considerations (Shinnar, 1988). This understanding enhances process synthesis techniques for determining process structures, represented as flowsheets and reactions, based on specified inputs and outputs (Patel et al., 2007).

The most efficient, productive and sustainable processes, must first be identified through the governing laws of thermodynamics. This is evidenced through the work of Tula et al. (2019), who described the software tool ProCAPD which used a hybrid approach to evaluate all feasible alternatives with a search space, Monjur et.al. (2021) describing the tool SPICE, which evaluates combinations of process building blocks rather than unit operations. SPICE also uses the minimisation of Gibbs Free Energy to determine the theoretical attainable limits for any reaction-separation system and, more recently Pazmiño-Mayorga et.al. (2022) developed a decision-making approach for the synthesis of reactive distillation systems using basic thermodynamic properties and kinetic data.

The development of flowsheets is governed by thermodynamics, where the change in G across a process, flow sheet, or operating unit is related to workflows or irreversibility. Similarly, the change in H corresponds to minimum or net heat flows in the processes. The Attainable Region (AR) approach, introduced by Horn (1964) and Glasser et al. (1987), provides a systematic method for developing and improving process flowsheets. In this paper, we extend the AR approach to determine both material and thermodynamically limited attainable regions.

* 1. Theoretical Development

This section follows the development and nomenclature used by Shinnar and Feng (1985). Consider a set of reactions involving N species, where a species j is denoted by and . We specify that must either be a feed to the process or reaction or alternatively be a product of the process or reaction. We can represent the set of species as vector ***A***T= {A1, A2…, AN} where ***A***T represents the transpose of vector ***A***. ***A*** must contain the species in the feed as well as all the species identified as possible products. Let be the number of moles of species . We can represent the composition of a mixture as vector ***n***T = {n1, n2, …, nN}.

Aris and Mah (1963) state that a set of chemical reactions is linearly independent if any of the reactions in the set cannot be written as a linear combination of the other reactions. Yin (1989) points out that the independent reactions may not correspond to actual reactions occurring in the system and are merely stoichiometric relationships between the chemical species in the system. In this paper, we have adopted the term Independent Material Balances (IMBs) to emphasise that individual relationships may not correspond to actual reactions in a process or reactor. We have denoted the number of IMBs that describe the relationship between the elements of ***A*** as S. The Gibbs stoichiometric rule gives an upper bound for S; different procedures to determine the IMBs have been reported, and we use the method of Yin (1989) in this paper.

We can define the stoichiometric matrix , with elements where and such that the S IMBs can be written as We define the extent vector ε of the S IMBs as ***ε***T= {ε1,ε2, …,εs}. The relationship between the molar composition of the reaction mixture , the initial or feed composition and the stoichiometric matrix is given by:

**,**  where the range of is such that all (1)

* + 1. Definition of the Material Balance Limited ARMB

The ARMB is the set of all possible outputs for a giventhat is consistent with the material balance constraints (that is, not taking other constraints such as kinetics, equilibrium, energy, etc. into account). This region contains all possible outputs from all possible processes or reactors that have a feed(s) of given composition and possible products of composition Thus, for a given feed :

iff for (2)

* + - 1. Properties of the ARMB

Some of the properties of the ARMB that will be used in this paper are:

* Consider two systems, one with a feed of***no1***and the second with a feed **no2,**where ARMB. This implies that, in principle, we can achieve from feed and conversely, we can achieve from feed ***.*** The vectors (and(are contained in the ARMB.
* We denote an extreme point e of the ARMB as ***E****e*(ARMB). We denote the set of all ***E***(ARMB) as {***E***(ARMB)}. The ARMB is the convex hull of {***E***(ARMB)}, and is an S dimensional polytope.
  + 1. Definition of the Thermodynamic Limited Attainable Region ART(T,p)

We begin by defining various properties that are useful in subsequent development. The specific enthalpy of component *Ai* in a mixture at temperature *T* and pressure *p* is denoted The specific enthalpies of ***A*** can be combined into vector Similarly, the specific Gibbs Free energy vector of ***A*** in a mixture at *T* and *p* is defined as where is the specific Gibbs Free energy of component *Ai*at T and p.

We define the Thermodynamic Limited Attainable Region with respect to feed, ART(**no**,T,p), as the set of *{H,G}* of all the products that can be achieved in a process or reaction from a given feed , where the feed and product enter and leave at *T* and *p*. Mathematically we can define the region as follows:

(3)

and {**Δ**H (*T, p*), **Δ**G (*T, p*)} ARMB.

* + - 1. Properties of the ARMB

The following can be deduced from this definition:

* ART is a linear transformation of the elements of ARMB. It follows that ART is a surjective mapping of the elements of ARMB, or equivalently that there is a one-to-many relationship between elements of ARMB and elements of ART. Consequently, ***E***(ARMB) are linearly transformed and are elements of ART (***no***,T,p)but may not be ***E***(ART (***no***,T,p)). However, all ***E***(ART (***no***,T,p)) correspond to ***E***(ARMB).
* We define the set of ***E***(ART (***no***,T,p)) as {***E***(ART (***no***,T,p))}. The {***E***(ARMB)} do not depend on either T or p. As T and/or p are changed, the {***E***(ART (***no***,T,p))} will be linear transformations of {***E***(ARMB)}, however, the {***E***(ART (***no***,T,p))} will depend on T and p. The implications of this will be discussed later.
* The ART is the convex hull of {***E*** (ART)}; thus the ART is a convex, connected set.
  1. Example: All possible material balances for conversion of biomass (glucose) into syngas, biogas and/or methanol

Consider a feed of 1 mole of glucose (C6H12O6) and 6 moles of water; we consider possible products CO, CO2, H2, CH3OH and CH4. We are thus considering the anaerobic conversion of glucose to the specified products. There are 4 IMB’s and the ***E***(ARMB) are given in Table 1. Thus, for example, E1 corresponds to the formation of CH4 and CO2, or biogas, E3 corresponds to a 1:2 mixture of CO2:H2 and E7 corresponds to a syngas mixture of CO:H2 of 1:1. Any point in the ARMB can be considered a feed point and thus the line between E7 and E1 corresponds to converting CO2 and H2 to glucose and water.

Table 1 Vertices of ARMB for a feed of 1 mole C6H12O6 and 6 moles H2O

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| IMB’s |  | E | ε1 | ε2 | ε3 | ε4 | Composition at Vertex |
| C6H12O6→6CO+6H2 | ε1 |
| 1 | 0 | 0 | 0 | 1 | 6H2O+3CH4+3CO2 |
| C6H12O6+6H2O→6CO2+12H2 | ε2 | 2 | 0 |  |  | 0 | 4H2O+4CH3OH+2CO2 |
| 3 | 0 | 1 | 0 | 0 | 12H2+6CO2 |
| C6H12O6+6H2→6CO3OH | ε3 | 4 |  |  | 0 |  | 4CO+8H2O+2CH4 |
| 5 |  | 0 |  | 0 | 3CO+6H2O+3CH3OH |
| C6H12O6→6CH4+3CO2 | ε4 | 6 | 0 | 0 | 0 | 0 | C6H12O6+6H2O |
| 7 | 1 | 0 | 0 | 0 | 6CO+6H2+6H2O |

The next step is to transform the ***E***(ARMB) to the {H,G} space and then find {***E***(ART)} by finding the convex hull of the transformed points, as shown in Fig 1. Ambient pressure is assumed in all 4 scenarios in Fig.1 and in (a) T=298K and H2O and CH3OH are liquid; in the three other figures, H2O and CH3OH are in the gas phase and (b) T= 548 K, (c) T=950K and (d) T=1300 K. The enthalpy of reaction (ΔHrxn) was assumed constant, and the Gibbs-Helmholtz relationship was used to calculate the temperature dependence of G.

We see that the boundary of the ART at 25 0C (Fig. 1(a)) with H2O and CH3OH as liquids is defined by 4 extreme points, namely E6,E1,E3, and E7. Changing the H2O and CH3OH to gas results in E4 moving the boundary of the region and furthermore, E1, E3, E4 and E7

being approximately linear in Fig. 1(b)..(d). Under the assumption of constant ΔHrxn, extreme points in ART remain in the boundary as the temperature varies, and only their relative positions change. Conversely, interior points do not move into the boundary of ART as temperature changes. Thus, G of the extreme points change with temperature, although H stay constant, resulting in the relative positions of E6 and the line between E1 and E7 changing with temperature.



Figure 1 {***E***(ART)} in the {H,G} space at different temperatures. Extreme points of the ARMB are shown; the numbers in rectangles correspond to the extreme points E in Table 1.

In Fig 1(a), G of E7 >0, implying that work needs to be added to convert glucose to syngas. G <0 of the other vertices, which allows us to conclude that these reactions could proceed for example, biologically. The anaerobic production of biogas is represented by the line between E6-E1. The production of hydrogen (E6-E3) releases less G, implying that there is less work available for the bacteria to use for metabolism and reproduction than those who produce CH4. G ≤0 for all E(AR) in Fig 1 (b) to Fig (d), which implies that thermo-catalytic reactions could potentially achieve the reactions between the feed and all possible products.

Minimum G corresponds to the thermodynamic equilibrium of the system. We can see that the overall system equilibrium changes from E1 (CH4 and CO2) at 298 K (Fig 1(a)) to E7 (syngas) at 1300 K (Fig 1(d)). At 950 K, the lower boundary of the ART is approximately a horizontal line containing E1, E4, E3 and E7. This means that the equilibrium conversion is determined by the mixing rather than the reaction term. Thus, practically, as the reaction proceeds to equilibrium, the composition will be path-dependent, and the resulting composition could look very different in different pieces of equipment, depending on how the reaction approaches equilibrium. This is indeed what is found in gasification and reforming reactions.

The conversion of CO2 and H2 can be studied by effectively moving the origin of the H-G axis of the ART to E3. Thus, the reaction for converting CO2 and H2 (E3)to methanol and water (E2), is represented by line E3-E2. We see that at typical reaction temperatures (Fig 1(b)) G>0, implying that work would need to be added to the reaction and that the per-pass conversion may be low if the work added by compression is limited. The effect of pressure can be included in the calculation but is beyond the scope of this paper.

* 1. Conclusions

A simple transformation of the extreme points of the ARMB is used to determine the ART. The ART is a 2-D representation of the heat and workflows or driving forces in a reaction or process, and the dimension does not increase with an increasing number of IMB’s or species. Process systems of any complexity can be drawn on a single 2-D axis, which offers considerable advantages in visualization, analysis and optimization that would otherwise be extremely complex using techniques that require analysis in n-dimensions.

The information contained in the ART is quite dense, and it can be used to investigate reactions, driving forces, and equilibrium in reactive systems. Process material and heat balances can be defined before a flow sheet even exists. This allows the laws of conservation to form the fundamental foundation of the design basis of process designs, allowing the design of the process with reduced CO2 emissions or that consume CO2.

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