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Attainable regions for a reactor: Application of ΔH–ΔG plot

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ABSTRACT

This paper describes a technique that can be used to analyze the reactions that take place in a reactor via mass balances, a graphical representation and interpretation of basic thermodynamic principles. This allows for the chemical species taking part in the reactions being considered, to create lines that define attainable boundaries in a GH plot. The end result is an attainable area that satisfies the conditions for an attainable region in a GH plot. The simultaneous methanol synthesis from syngas with the Water Gas Shift (WGS) reaction is used to illustrate this approach. Considering the investigation, one can readily see that at higher temperatures the reaction was not feasible thermodynamically at 1 bar, but at increased pressure the reaction could again become favorable and thermodynamically feasible. This paper also shows that the introduction of either water or CO_2, or both, to the feed opens up the mass balance region, resulting in WGS activity and generating more reaction path alternatives. Again, the change in Gibbs free energy across the reactor and the reaction pathways leading to product are interlinked.

Keywords: Attainable region; Chemical reactors; Chemical species; Mass balance; Methanol synthesis

1. Introduction

The performance of chemical reactors is of paramount interest to chemical engineers, because it is the heart of any chemical process through which raw materials are converted into the desired products. The analysis of chemical systems in which chemical reactions take place (chemical reactors), is achieved by studying the behavior of the chemical species reacting in the system so as to evaluate operating parameters, such as temperature and pressure, which affect the overall process (Hill, 1977; Patel et al., 2005).

The methodical examination of chemical reactions started with Damkohler's work on reactions and mass transfer in Germany in the 1930s and 1940s. Van Heerden in Holland studied temperature variations in reactors (Sachmidt, 1998). Denbigh (1956) first drew attention to the use of the second law of thermodynamics as important to chemical reactor and process design. Since then, many other researchers have published reports on the same subject (Aris and Mah, 1963; Berg, 1980; Hendry et al., 1973; Nishida et al., 1981; Riekert, 1974; Rotstein et al., 1982; Shinnar et al., 1981, 1982; Shinnar, 1988; Shinnar and Feng, 1985; Stephanopoulos and Townsend, 1986; Umeda et al., 1979). In 1976 May and Rudd proposed a method to synthesize thermodynamically feasible Solvay clusters using the principle of mass conservation, and the conditions imposed on the free energy change of reaction. This led to the testing of the thermodynamic feasibility of a reaction on a single free energy reaction diagram, as long as the reaction can form a nested polygon that exhibits the appropriate model of free energy differences intersections (May and Rudd, 1976). Since then several works have been published on the subject. Among them the works of Rotstein et al. (1982), Stephanopoulos et al. (1982), and Stephanopoulos and Townsend (1986), whose research was on the systematic development of new reaction paths via different techniques. The synthesis approach they presented was based on using algebraic and thermodynamic tests to screen out alternative reaction schemes that were unacceptable on the grounds of low equilibrium conversion. Stephanopoulos and associates posited the thermodynamic properties of reactions as the basis of path synthesis (Brown et al., 1991; Peng et al., 1997). In addition, Rotstein et al. (1982) made a technical advance in identifying some 'topological or algebraic properties' that chemical reactions share within the Gibbs free energy change

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