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Learning on chemical equilibrium shift assessment for membrane reactors using Gibbs free energy minimization method

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ABSTRACT

This work presents how to deal with calculations of equilibrium shift in a membrane reactor using Gibbs free energy minimization method. Students are required to use the thermo-dynamic relations, stoichiometric table for membrane-assisted process, reliable physical property databases, optimization tools and mass balances fundamentals. As an example, catalytic dehydrogenation of cyclohexane, relevant for hydrogen storage and supply, was solved using MatLab® software. The equilibrium shift conversion as well as the influence of membrane reactor operational parameters were clearly demonstrated. Simulation results were successfully compared with the experimental data previously published in open literature. Thus, this exercise can help undergraduate students of chemical engineering to master the complex issues involved in chemical equilibrium calculations, offering them an opportunity to practice the application of modern numerical problem-solving tools for reacting systems.

1. Introduction

Chemical equilibrium is a subject that many students find hard to learn and some instructors find difficult to teach. The most common problems (van Driel and Grüber, 2003; Doymus, 2008; Castier and Amer, 2011), associated with an understanding of chemical equilibrium, include: (i) misconceptions on the idea of chemical equilibrium (*v.g.*, learners failure to comprehend the dynamic nature of chemical equilibrium, viewing it as a "nothing happening" state); (ii) nature of chemical equilibrium (*v.g.*, students consider the equilibrium as somehow involving two disconnected sides of the reaction); (iii)

explanation and prediction of changes occurring in chemical equilibrium (*v.g.*, learners display resistance to both the implementation/interpretation of mathematical expressions and to their solution using modern numerical problem-solving tools). In general, these issues can be related to student's conceptual problems with the abstract perceptions of chemical equilibrium. Additional difficulties arise if the studied system involves simultaneous reaction and separation (*v.g.*, learners misjudge that a membrane affects the rates of the forward and reverse reactions by withdrawing selectively one of the reaction products). In order to overcome these learning difficulties, some teaching approaches can be suggested: (i) to present reversible and incomplete chemical conversions (*v.g.*,

Nomenclature

a_i	Activity of component i
F_i	Molar flow of component i entering the reactor, mol/h
G_{Total}	Gibbs free energy, J
$\overline{G_{Total}}$	Gibbs free energy per total number of mols, $\frac{G_{Total}}{n_T}$, J/mol
G_i	Gibbs free energy, J
P	Total pressure, Pa
P_0	Pressure in a standard state, Pa
R	Gas constant, Eqs. (2), (5) and (6), J/mol K
S	Ratio between the molar flow of sweep gas to molar flow of cyclohexane entering the reactor
T	Temperature, K
X_1	Fraction of cyclohexane converted
X_2	Amount of benzene permeated through the membrane relative to the amount of cyclohexane fed
X_3	Amount of hydrogen permeated through the membrane relative to the amount of cyclohexane fed
y_i	Gas phase mole fraction
μ_i	Chemical potential of i species
$\emptyset_i$	Activity coefficient

exploratory discussions on systems in which a reversible reaction occurs); (ii) to introduce the dynamic equilibrium concept (*v.g.*, the use of analogies or metaphors of dynamic equilibriums, in terms of oscillating systems); (iii) to discuss the Le Chatelier's principle (*v.g.*, qualitative account for changes in chemical equilibrium), (iv) to explain different roles of membrane (v.g., separation, simultaneous reaction and separation, and/or reactive interface functions). Thus, it can be easier to analyze and to understand the potential of emerging technologies, as membrane systems, basing on the thermodynamics concepts.

Membrane reactors have been successfully used for several reversible chemical equilibrium limited reactions, among them dehydrogenation (Khademi et al., 2010), esterification (Park et al., 2011; Osorio-Viana et al., 2014; Gómez-García et al., 2016, 2017), partial oxidation (Guilbert et al., 2015), etc... Several membrane reactor configurations have also been proposed. In some of them, the membrane provides only a separation function (Gómez-García et al., 2016); in some others, it affords simultaneously the reaction and separation (Khajavi et al., 2010) or makes available a reactive interface (Yu et al., 2009). Thus, a number of experimental devises and mathematical models have been proposed for the configuration, analysis, and design of membrane reactors (Seidel-Morgenstern, 2010; Diban et al., 2013).

The highest conversion that can be achieved in reversible reactions is the equilibrium one. It represents a constraint for reactor performance. Indeed, some reactions require high temperature and pressure to take place in a considerable extent (Shacham and Brauner, 2015). Le Chatelier's principle states that change in temperature, pressure or concentration of reactants in an equilibrated system will stimulate a response that partially offset the change to establish a new equilibrium. In the case of membrane reactors, products can be removed from the reaction section (through the membrane)

forcing the equilibrium of the reaction "to the right", permitting to get more product (Fogler, 2016).

Two teaching approaches, involving chemical kinetics and thermodynamics, have been proposed in the literature to predict the equilibrium shift that can be achieved using membrane reactors. Within a kinetic framework, the equilibrium is based on zero overall reaction rate and corresponding reaction rate equation (law). In an early attempt, Mohan and Govind (1988) used a plug-flow membrane reactor (PFMR) model to predict the behavior of five different reversible dehydrogenation reactions. They analyzed the profiles of conversion *vs.* rector length choosing the hydrogen asymptotic value as that corresponding to the equilibrium conversion. Next, Abashar and Al-Rabiah (2005) also considered similar methodology for the production of ethylene and cyclohexane in a PFMR. Itoh (1991, 1995) proposed an improved kinetic approach. He calculated the maximum conversion in a PFMR, solving the hydrogen balances simultaneously with the constraint of equal hydrogen pressures on both sides of membrane. Finally, Barbieri et al. (2001) used a tank in series model, which implied the removal of hydrogen until its partial pressure remained equal on both sides of the membrane. Notice that the application of this methodology requires the accessibility to kinetic reaction rate expression that is not always available.

From a thermodynamic perspective, equilibrium is defined as a state of minimum free energy. Its description is based on two approaches (rigorously, containing activities): (i) the stoichiometric equation and thermodynamic equilibrium constant; or (ii) the total Gibbs energy minimization. These two methodologies let to obtain the same numerical answer. In the first case, different stoichiometric equations of the same chemical expression let to obtain different values of thermodynamic equilibrium constant; however, equilibrium composition is independent on selected stoichiometric equation (Pekař, 2011). At first, Rezai and Traa (2008) proposed the equilibrium constant thermodynamic model, together with the equality of hydrogen partial pressures on the reaction and permeation sides as constraint, for dehydrogenation equilibrium shift calculations in membrane reactors. This methodology was also used for the analysis of *n*-butane conversion to isobutene (Al-Megren et al., 2013), synthesis of ethyl lactate (Collazos et al., 2013) and production of methyl acetate (López-Zamora et al., 2013). In the second case, two variations exist: the stoichiometric and the non-stoichiometric (*e.g.*, each species can be treated independently without specifying a set of reactions *a priori*) ones. Notice that thermodynamic approach is a predictive one (the values of thermodynamic parameters can be found in databases such as NIST (https://webbook.nist.gov), DIPPR (https://dippr.byu.edu), or Poling et al. (2000)). Moreover, if neither kinetics nor reaction stoichiometry is known, the non-stoichiometric total Gibbs energy minimization method becomes the only one alternative for equilibrium calculation.

This work presents how to deal with calculations of equilibrium shift in a membrane reactor using the Gibbs free energy minimization stoichiometric method. Students are required to use the thermodynamic relations, stoichiometric table for membrane-assisted process, reliable physical property databases, optimization tools and mass balances fundamentals. As an example, catalytic dehydrogenation of cyclohexane, relevant for hydrogen storage and supply (Koutsonikolas et al., 2012), is solved using MatLab® software. The obtained results are in good agreement with the experimental data previously published in open literature