



Probability density distribution in the prediction of reaction equilibria



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ABSTRACT

Reaction equilibria play an important role in chemical engineering. They can be calculated from substance properties of the compounds involved in the reaction. Since these substance properties usually come from measurements there is always an uncertainty with them. This uncertainty in the input data causes an uncertainty of the simulation results, even if the model itself is perfect. The effect of input uncertainty on uncertainty in equilibrium calculations has been studied. Monte Carlo sampling has been applied for accessing uncertainty and probability density distribution. Uncertainty in equilibrium conversion can be very high. However, the shape of the curve of equilibrium conversion over temperature can be predicted very precisely. As a consequence, simulations of reaction equilibria can still be useful, because temperatures required for achieving a certain conversion can be determined with comparatively high accuracy. The probability density distributions of the obtained equilibria can strongly deviate from those of the input data and in some cases can even become bimodal.

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1. Introduction

Reaction equilibria constitute an important limit for the conversion in many chemical processes. A famous example for a technical reaction that is affected by the reaction equilibrium is the synthesis of ammonia. Utilization reactions for CO₂ [1] or esterification [2] are also often restricted by the reaction equilibrium. Another example is the absorption of CO₂ from flue or bio gas by a solvent that undergoes a chemical reaction with CO₂ to enhance its solubility. The maximum amount of CO₂ that can be solved at certain conditions is determined by the reaction equilibrium [3,4].

Knowledge about reaction equilibrium is crucial for the design of processes. Measuring them can be challenging, because reactions slow down when approaching the equilibrium. Consequently, reactions do not reach the equilibrium but (in best case) only get close to it. Based on knowledge about some pure substance properties, it is possible to obtain the position of the reaction equilibrium without performing the reaction. This allows avoiding time-consuming and expensive experimental work on reactions that are thermodynamically not feasible. These results can also be interesting for catalysis research, to find out how far the reaction is away from equilibrium.

Like the accuracy of every measurement, the accuracy of

calculation results is also limited. Assuming that the calculations are done correctly, there are still two factors causing uncertainty in simulations results: 1.) deviations of the applied models from reality and 2.) uncertainties of the input data (i.e. in this case the substances properties). If the laws of thermodynamics are valid descriptions of reality (which seems to be a reasonable assumption), calculation of reaction and phase equilibria in principle should not suffer from uncertainties due to the model. Nevertheless, these calculations use parameters like fugacity and activity coefficients. These have a sound thermodynamic basis, but the models used for their estimation are never perfect. Nonetheless, in most cases uncertainty is dominated by the uncertainty of substance properties used in the calculation. Every phase and reaction equilibrium calculation is based on data obtained experimentally. Even if the input data are obtained from other simulation, these other models at some point have been fitted to experimental data. Each experimental value carries an uncertainty. Since these input data are not absolutely accurate, the simulation results cannot be absolutely accurate themselves. A review on the sensitivity of calculation results on input data was presented by Saltelli et al. [5].

In contrast to the uncertainties of experimental values, those of simulation results are often not evaluated. Asprión et al. [6] studied the effect of uncertainties on the robustness of process design. Evans et al. [7] evaluated the uncertainty in stochastic models for the kinetics of chemical reactions. Another study on reaction kinetics has been done by Albrecht [8], who estimated the uncertainties in model parameters. It was observed that the

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probability density distribution of the parameters often strongly varies from normal distribution. It was concluded that a Monte-Carlo analysis was suited to describe these uncertainties. Van Kampen [9] described the mathematics of probability distribution for chemical reactions occurring in one-phase systems. The rate constants were related by the law of mass action and it was demonstrated that partition functions for the molecules resample a Poisson distribution, even though they are not identical to it. Schechner and Driscoll [10] presented a study on the uncertainty of equilibrium calculations within acidification models for depositions of soils and drainage water. They took into account the uncertainty of measurements and their effect on the modeling results. However, the values of the substance properties themselves were assumed to be precise and their uncertainty was thus neglected. Panagiotopoulos et al. [11] calculated phase equilibria from Monte-Carlo simulations and assigned deviation between ten different runs as an uncertainty to their results. However, this approach does not access the total uncertainty, since it is based on the assumption that the applied Monte-Carlo model is perfect (i.e. would produce an absolutely accurate result if the number of samples becomes infinite). Cabaniss [12] evaluated the probability density distributions for the results of solubility calculations. Solubilities of metal ions were modeled depending on pH value. It was observed that the probability density distributions for solubility is often heavily skewed and thus strongly deviates from normal distribution. For some pH values even a bimodal probability density distribution was observed for the solubility of Al^{3+} . This means that likelihood is higher for a solubility higher as well as lower than the expected solubility. Sin et al. [13] studied the influence of uncertainties in a huge number of parameters, including equilibrium constants, on process analytical technology in bioprocess engineering. They analyzed the effect of input uncertainty on the output uncertainty using a Monte-Carlo sampling approach. However, the uncertainty of the input data was only categorized in three groups (low: 5%; medium: 25%; high: 50%) based on an expert review. Grob and Hasse [14] studied the reaction equilibrium of an esterification reaction, which show a superimposed liquid-liquid phase equilibrium. Based on the measurements, they derived pseudoreaction equilibrium constants for which they determined uncertainties. However, to the best of our knowledge no study on the uncertainty of predictive reaction equilibria modeling and especially not the underlying probability density distribution has been published so far.

This work aims at the uncertainty related to calculations of reaction equilibria (with superimposed phase equilibria) induced by uncertainties in the substance properties used as input parameters. The discussion is based on the example of the dehydrogenation reaction of hydrogenated Liquid Organic Hydrogen Carriers (LOHC). These are organic compounds that can take up hydrogen through chemical bonds and store it at ambient conditions. The hydrogen is released by dehydrogenation at elevated temperatures and moderate pressure [15–17]. A special focus is thereby set on the shape of the probability density function. The question if the expectancy value is actually the most probable value and if not, how it deviates from the most probable value is analyzed. A Monte-Carlo sampling approach is used in this study. This should not be confused with Monte-Carlo methods in molecular simulations, which are used to determine properties of substances and mixtures.

2. Modeling

2.1. Equilibrium calculation and input parameters

The basis for calculations of reaction equilibria is the Gibbs energy of reaction $\Delta^R g$, which can be derived from the enthalpy of

formation and the entropy of the compounds involved in the reaction. The Gibbs energy of reaction determines the equilibrium constant K [18].

$$\ln K = -\frac{\Delta^R g}{RT} \quad (1)$$

If the equilibrium constant is known, the composition can be calculated for a given starting composition. However, this is only possible in one-phase systems. Many reactions proceed in systems where a second phase is present. If the system is in equilibrium, not only the reaction is in equilibrium, but also the two phases. This phase equilibrium can significantly influence the reaction equilibrium. Superimposed liquid-liquid and vapor-liquid (or gas-liquid) equilibria occur in many reaction systems. The vapor-liquid equilibrium can be described by equation (2) for each compound i individually:

$$y_i \cdot \varphi_i \cdot P = x_i \cdot \gamma_i \cdot P_{0i}^{LV} \cdot \varphi_{0i}^{LV} \cdot \Pi_{0i} \quad (2)$$

where y_i and x_i are the mole fractions of compound i in the vapor and the liquid phase, φ_i and φ_{0i}^{LV} are the fugacity coefficients of the respective compound in the vapor phase and of the pure compound on the boiling point curve, respectively, γ_i is the activity coefficient of the compound, P_{0i}^{LV} is its saturated vapor pressure, Π_{0i} is the Poynting correction from P_{0i}^{LV} to P and the P is the system pressure.

The position of the reaction equilibrium at given conditions can thus be calculated if a number of substance properties are available. These are

- the enthalpies of formation,
- the entropies (of formation),
- the heat capacities,
- saturated vapor pressures,
- an equation of state (and the respective input parameter),
- a g^E -model (and the respective input parameter),
- molar volume of pure compounds in the liquid state.

The first two are required to calculate the Gibbs energy of reaction and thus the equilibrium constant. Since they are usually tabulated at standard conditions, it is required to convert them to reaction temperature. If the temperature difference between standard and reaction conditions is not negligibly small, heat capacities of all compounds need to be known. These data are sufficient if the reaction is performed in an one-phase system at moderate pressures. If e.g. a vapor-liquid equilibrium occurs, the saturated vapor pressures are needed, since they mainly determine the phase ratio. For ideal systems these data are sufficient. However, real systems often deviate from ideal behavior and fugacity and activity coefficients therefore have to be taken into account.

If there is a gas/vapor phase present an appropriate equation of state (EoS) is needed to describe its non-ideality and to calculate the fugacity coefficients. The input data required depend on the respective EoS. Often parameters such as critical temperature, critical pressure, acentric factor and interaction parameters between different compounds are needed.

If there is a liquid phase present, a g^E -model is often used to describe its non-ideality and calculate the activity coefficients. Most g^E -models require interaction parameters between all compounds. Some models such as UNIFAC [19] or COSMO-RS [20] are able to predict activity coefficients based only on the molecular structures. An alternative to g^E -models for the calculation of activity coefficients are some EoS like PC-SAFT. The effects of non-ideality in the liquid phase should not be neglected. This is also the reason for influences of different solvents on reaction equilibria, which can

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