////Title: Traditional Equilibrium Models Lead to Inaccurate Predictions

////Stand-first:

Equilibrium is the cornerstone of industrial chemical processes, especially when optimising chemical production. But what if the equilibrium models that engineers use to predict product yields under different conditions were fundamentally inaccurate? Dr Yousef Haseli (has-el-ee) of Central Michigan University has found that there can often be a large discrepancy between expected and actual results, and that this is because common equilibrium models are flawed from the outset.

////Body text:

During chemical manufacturing, an industrial chemist will begin with starting substances that they wish to combine in a reaction vessel to form a desired chemical. The starting substances are known as 'reactants', while the substances that are formed are known as 'products'. As a chemical reaction proceeds, products are continually formed. But not all of the reactants are converted into products. Rather, the products themselves can undergo another chemical reaction to transform back into reactants.

Eventually, however, the mixture in the reaction vessel reaches a state known as 'equilibrium'. At equilibrium, the forward reaction, where reactants are converted into products, and the reverse reaction, where products transform back into reactants, proceed at equal rates. Thus, at equilibrium, there is no change in the overall quantity of products or reactants.

Industrial chemists are very interested in equilibrium. That's because they have a vested interest in the amount of product that exists at this end-state of the reaction, as they intend to sell it or use it for some other purpose. An accurate computer model of equilibrium conditions can help a chemist to manipulate a given reaction to achieve more product at equilibrium, using the least amount of energy and materials.

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Consider a real-world example.

We hear much about hydrogen gas as an alternate fuel for vehicles – one that is emissions-free. Sounds appealing, right? The problem is that hydrogen gas does not exist in nature as a stable substance; it needs to be derived from water, or from hydrocarbons such as methane. However, deriving hydrogen gas from methane is an intricate and challenging process.

One method for producing hydrogen is known as the 'methane steam reforming' method. During this process, methane reacts with steam under high temperature, in the presence of a catalyst, to produce hydrogen, carbon monoxide, and a relatively small amount of carbon dioxide. This combination of gases is often referred to as 'syngas'.

As mentioned, chemists want to achieve the greatest amount of product – in this case, hydrogen gas for use in renewable technologies. They also want to minimise waste. Speaking in broader terms, more accurate computer models could save a chemical company significant amounts of time and money, making hydrogen gas more viable as a sustainable fuel. Because extremely high temperatures and pressures are sometimes used in chemical manufacturing, a better understanding of equilibrium conditions can also have implications in terms of workplace health and safety.

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Dr Yousef Haseli is an Assistant Professor at the School of Engineering and Technology, Central Michigan University. For over a decade, he has conducted research on various subjects in the field of thermofluids and energy sciences.

In the case of methane steam reforming, Dr Haseli notes that complex models have been developed to theoretically optimise the process. However, in a recent literature survey, he made a startling discovery. He found a significant level of inaccuracy in the results gained from commonly-used equilibrium models. Specifically, he observed a large discrepancy between expected and actual results for equilibrium concentrations of reactants and products in methane steam reforming.

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Equilibrium models include a component known as the 'Gibbs function'. When the Gibbs function reaches zero, then the reaction is deemed to be at equilibrium, and the concentrations of both products and reactants are relatively fixed (provided the reaction conditions are kept constant). These concentrations are what industrial chemists are very much interested in.

Traditional methods of predicting the Gibbs function at equilibrium, however, have routinely fallen short. That is, there is a discrepancy between expected yields, based on the equilibrium calculations, and what they actually get. Put simply, the mathematical predictions are not indicative of what happens in the real world. They are merely predictions based on what should happen in ideal circumstances. In reality, the reaction is a far more dynamic process.

So how can this challenge be overcome? Is there another type of model that is able to make more accurate predictions?

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Dr Haseli suggests that equilibrium conditions can be more correctly simulated using so-called 'kinetic modelling'.

In simple terms, kinetics looks at how fast a reaction occurs. Temperature increases reaction rates, because heat makes atoms and molecules move around faster. As a result, they are more likely to collide and react. For example, when a pan is incredibly hot, the food being cooked in it browns and chars, undergoing a chemical reaction, very quickly. This is an everyday example of kinetics at play – the increase in temperature causes a change in the reaction rate.

With that in mind, kinetic *modelling* of equilibrium likewise focuses on the relationship between temperature and reaction rate. This approach allows one to factor in the *actual* conditions of the system at any given time. As Dr Haseli highlights, an accurate model of methane steam reforming, for example, should include the kinetics of the reactions involved. Kinetic modelling is more adapted to the dynamic nature of reactions.

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The failure of equilibrium models to accurately predict the outcome of a reaction has significant implications. In the case of methane steam reforming, the predicted quantities of the desired products may be overestimated. In a competitive market, these discrepancies could mean lots of wasted time and money for chemical companies.

So, whether it be producing a certain medicine, an industrial chemical or a sustainable fuel such as hydrogen gas, kinetic modelling will be the key to success – as far as chemical equilibrium is concerned anyway.

Meet the Researcher

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