

# Guide to Approach-to-Equilibrium

## Approach-to-Equilibrium

Approach-to-Equilibrium (ATE) indicates how close a reaction is to its equilibrium position by measuring the distance between the equilibrium position (maximum achievable conversion under a given set of conditions) and the achieved conversion at the unit outlet conditions. ATE is shown in temperature units, with an ATE of zero indicating that the reaction is at equilibrium. It is worth noting that changes in operating conditions will have an effect on the conversion of the catalytic reaction, sometimes better conversion, sometimes worse conversion. Examples of these conditions are, temperature, pressure, feed rate (space velocity), concentrations of reactants and products. These changes will have an effect on the equilibrium position and hence an impact on ATE.

## ATE in the steam methane reforming reaction

The steam reforming of methane ( $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3 \text{H}_2 + \text{CO}$ ) is an endothermic reaction which undergoes volumetric expansion, meaning that high operating temperature and low pressure provides a more favourable equilibrium position for higher conversion to hydrogen and CO.

Figure 1 depicts the  $\text{CH}_4$  slip at equilibrium (equilibrium  $\text{CH}_4$  - blue line) and the actual  $\text{CH}_4$  slip (reaction profile - red line) as a function of reformer tube outlet temperature for a given set of operating conditions. The ATE is the horizontal distance between both lines measured at catalyst tube outlet. As Figure 1 indicates, at low temperatures the ATE tends to increase; whereas at high temperatures the reaction profile tends to approach

the equilibrium curve eventually approaching close to equilibrium (ATE =  $0^\circ\text{C}$ ). Note that the reaction profile curve will never cross-over the equilibrium curve (meaning that the ATE will never be less than  $0^\circ\text{C}$ ).

In steam reforming catalysts ATE is normally close to, but rarely zero, at start-of-run, and it increases gradually as the catalyst ages. In the example given in Figure 1 at the tube outlet temperature of  $808^\circ\text{C}$  the  $\text{CH}_4$  slip is 4.60 mol%; however, that  $\text{CH}_4$  slip corresponds to an equilibrium temperature of  $796^\circ\text{C}$ , hence the ATE =  $12^\circ\text{C}$ .

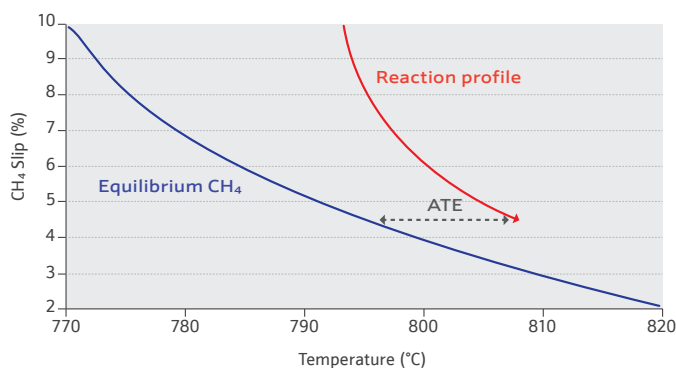


Figure 1: Representative reaction profile compared to the equilibrium line. This equilibrium curve is nominal – it will vary according to pressure and steam-to-carbon ratio.

Lastly, it should be noted that the true tube outlet temperature is difficult to measure, this value is normally inferred from the nearest thermocouple reading by assuming a heat loss. This assumption will invariably affect the final value of the ATE. If the assumed heat loss is too great, an artificially high ATE will be reported, and vice versa.

## ATE in the water gas shift reaction

The water gas shift (WGS) reaction ( $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$ ) is an equimolar exothermic reaction, meaning that low operating temperatures will provide a more favorable equilibrium position for conversion to hydrogen and  $\text{CO}_2$  whilst altering the pressure will have no effect.

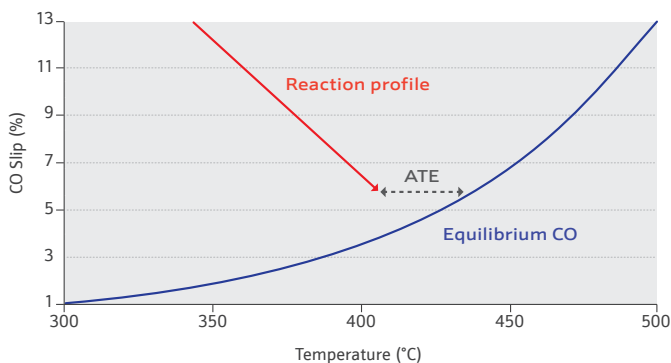


Figure 2: Representative reaction profile compared to the equilibrium line. This equilibrium curve is nominal – it will vary according to the steam-to-dry gas ratio.

Figure 2 shows the CO at equilibrium (equilibrium CO – blue line) at a given set of operating conditions and the CO slip (reaction profile – red line) as function of temperature. Again the ATE is the horizontal distance between both lines measured at catalyst bed outlet conditions. In this reaction a competitive effect between kinetics (favoured by increasing temperature) and equilibrium position (favoured by decreasing temperature) occurs. This means that when using JM catalysts the inlet temperature can be optimised using JM kinetic modelling software.

The ATE generated by a high temperature shift converter is relatively higher than other forms of shift converter. However, the ATE in all shift converter types is expected to gradually increase as the catalyst deactivates.