Equilibrium Constant in a Reaction rate in a PFR Reactors
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- In this session you will learn how to use equilibrium constants within a reaction rate expression.

Application of Chemical Equilibrium to the Production of Styrene

Styrene is a monomer used in the production of many plastics. It has the fourth highest production rate behind the monomers of ethylene, vinyl chloride and propylene. Styrene is made from the dehydrogenation of ethylbenzene:

$$C_6H_5{-}C_2H_5 \Leftrightarrow C_6H_5{-}CH = CH_2 + H_2 \qquad (1)$$

The conversion of ethylbenzene to styrene given by reaction 1 is limited by equilibrium. As can be seen in Figure 1, the equilibrium conversion increases with temperature. In addition, if an inert species such as steam is added the equilibrium increases. For example at 880 K, the equilibrium conversion is 0.374 and if steam at 10 times the molar flowrate of ethylbenzene is added the conversion increases to 0.725. Why does this happen? How could you have discovered this?

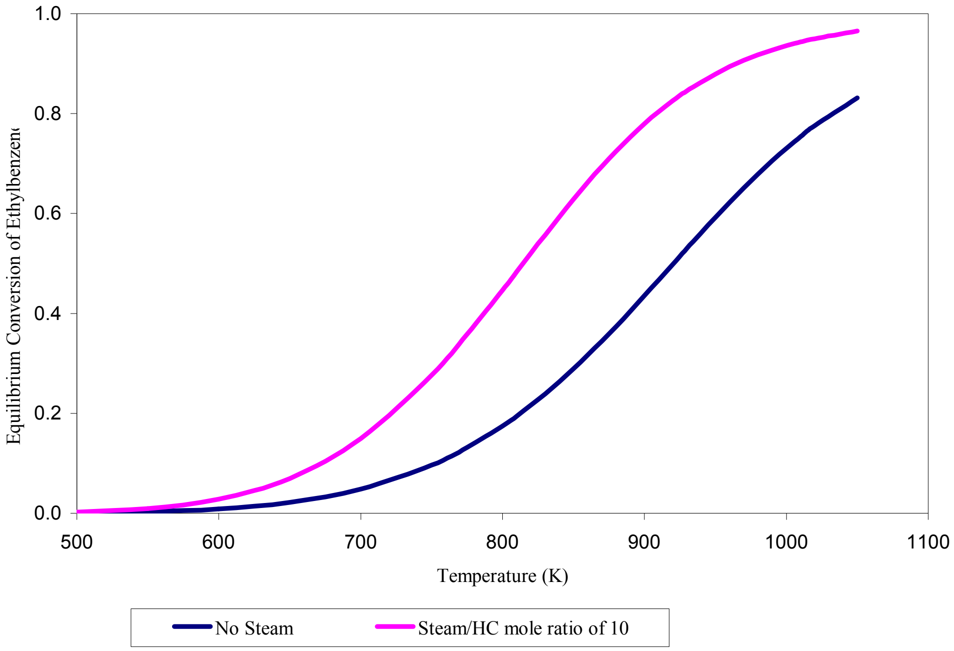

Figure 1: The effect of Temperature and Steam on the Equilibrium Conversion of Ethylbenzene to Styrene. The pressure is 1.36 atm, and the initial flowrate of ethylbenzene is 152.2 mol/s

The reaction rate expression that we will use in this discussion is from Hermann[1]:

$$r_{EB} = -7.491\times 10^{-2}\,\frac{\text{mol EB}}{\text{g}_{\text{cat}}\text{s kPa}}\exp\left[-\frac{21874\ \text{cal/mol}}{\left(1.987\,\frac{\text{cal}}{\text{mol K}}\right)T}\right]\left(p_{EB}-\frac{p_{Styrene}p_{H_2}}{K_P}\right) \tag{2}$$

Notice that the reaction rate has units and that the concentration term is partial pressure with units of kPa.

Equilibrium - Theory

For most reactions you will need to input the equilibrium constant as a function of temperature. The equilibrium constant is defined by equation as

$$K = \exp\left(\frac{-\Delta G_{rxn}}{RT}\right) \tag{3}$$

for the stoichiometry given by equation 1 the equilibrium constant is defined in terms of activities as

$$K = \frac{a_{styrene}a_{H_2}}{a_{EB}} \tag{4}$$

for a gas the activity of a species is defined in terms of its fugacity

$$a_i = \frac{f_i}{f_i^0} = \frac{f_i}{1\,\text{atm}} = \gamma_i p_i \tag{5}$$

where γ_i has units of atm^{-1}.

Now combining equations 3, 4, and 5 results in the following for our stoichiometry given in equation 1,

$$K_P = \exp\left(\frac{-\Delta G_{rxn}}{RT}\right)\text{atm} \tag{6}$$

It is very important to note that the calculated value of K_p will have units and that the units are 1 atm, based on the standard states for gases.

To predict ΔG_{rxn} as a function of temperature we will use the fully integrated van't Hoff equation given in by Fogler[2] in Appendix C as

$$\ln\frac{K_P\big|_T}{K_P\big|_{T_R}} = \frac{\Delta H_R^o\big|_{T_R} - T_R\Delta\hat{C}_p}{R}\left(\frac{1}{T_R}-\frac{1}{T}\right)+\frac{\Delta\hat{C}_p}{R}\ln\left(\frac{T}{T_R}\right) \tag{7}$$

Now we can predict $K_P\big|_T$ as a function of temperature knowing only the heat of reaction at standard conditions (usually 25°C and 1 atm and not STP!) and the heat capacity as a function of temperature. What is assumed in this equation is that all species are in one phase, either all gas or all vapor. For this Styrene reactor all of the species will be assumed to be in the gas phase and the following modification of equation 7 will be used

$$\ln\frac{K_P\big|_T}{K_P\big|_{T_R}} = \frac{\Delta H_R^o\big|_{T_R}^{vapor} - T_R\Delta\hat{C}_p^{vapor}}{R}\left(\frac{1}{T_R}-\frac{1}{T}\right)+\frac{\Delta\hat{C}_p^{vapor}}{R}\ln\left(\frac{T}{T_R}\right) \tag{8}$$

The heat capacity term is defined as

$$\hat{C}_p^{vapor} = \frac{\int_{T_R}^{T} C_p^{vapor}\,\mathrm{d}T}{\left(T - T_R\right)} \tag{9}$$

and for the above stoichiometry

$$\Delta\hat{C}_p^{vapor} = \hat{C}_{p_{styrene}}^{vapor} + \hat{C}_{p_{H_2}}^{vapor} - \hat{C}_{p_{EB}}^{vapor} \tag{10}$$

Now for some hand calculations!

To determine the equilibrium conversion for this reaction we substitute equation 5 into equation 4 yielding

$$K_P = \frac{p_{styrene}\,p_{H_2}}{p_{EB}} \tag{11}$$

Defining the conversion based on ethylbenzene (EB) and defining the partial pressure in terms of a molar flowrate gives:

$$p_i = \frac{F_i}{F_T}P = \frac{\left(F_{i_0} - F_{EB_0}\chi_{EB}\right)}{F_T}P \tag{12}$$

Substituting equation 12 for each species into equation 11 with the feed stream consisting of no products and then simplifying gives

$$K_P = \frac{P}{F_T}\left(\frac{F_{EB_0}\chi_{EB}^2}{1-\chi_{EB}}\right) \tag{13}$$

where the total molar flow is the summation of all of the species flowrates and is given by

$$F_T = F_{EB} + F_{styrene} + F_{H_2} + F_{steam} \tag{14}$$

With the use of a stoichiometry table the total flowrate can be defined in terms of conversion as

$$F_T = F_{EB_0} + F_{steam_0} + F_{EB_0}\chi_{EB} \tag{15}$$

Substituting equation 15 into equation 13 gives the following equation

$$K_P = \frac{P}{\left(F_{T0} + F_{EB_0}\chi_{EB}\right)}\left(\frac{F_{EB_0}\chi_{EB}^2}{1-\chi_{EB}}\right) \tag{16}$$

The above equation can be solved using the quadratic equation formula and is

$$\chi_{EB} = \frac{-K_P F_{steam_0} + \sqrt{\left(K_P F_{steam_0}\right)^2 + 4F_{EB_0}\left(P + K_P\right)K_P F_{T0}}}{2F_{EB_0}\left(P + K_P\right)} \tag{17}$$

There are two very important aspects to Styrene reactor operation that can be deduced from equation 13 or 16. Knowing that at a given temperature K_p is a constant then

1. Increasing the total pressure, P, will decrease χ_{EB}
2. Increasing the total molar flowrate by adding an inert such as steam will increase χ_{EB}

The following page gives sample calculations for all of the above. From these sample calculations at a temperature of 880 K the equilibrium constant is 0.221 atm. At an inlet flowrate of 152.2 mol ethylbenzene/s and no steam the conversion is 0.372. At an inlet flowrate of 152.2 mol ethylbenzene/s and a steam flowrate of 10 times the molar flowrate of ethylbenzene the conversion increases to 0.723.

Equilibrium Calc.

CASE 1 No steam

$F_{EB_0} = 152.2$ mol/s

$F_{steam_0} = 0$

$P_0 = 1.378$ atm

$T = 880$ K
$K_p = 0.221$ atm

CASE 2 steam

$F_{EB_0} = 152.2$ mol/s

$F_{steam_0} = 1522$ mol/s

$$\frac{F_{steam}}{F_{EB}} = 10$$

$P_0 = 1.378$ atm
$T = 880$ K
$K_p = 0.221$ atm

for CASE 1 No Steam

$$X = \frac{0 \pm \sqrt{0 + 4\left(152.2\frac{mol}{s}\right)(1.378\,atm + 0.221\,atm)(0.221\,atm)\,152.2\frac{mol}{s}}}{2\,(152.2\,mol/s)(1.378\,atm + 0.221\,atm)}$$

$$\boxed{X = 0.372 \quad (\text{No Steam})}$$

for CASE 2 with steam/HC = 10

$$X = \frac{-(0.221\,atm)\left(1522\frac{mol}{s}\right) \pm \left[\left(0.221\,atm\ 1522\frac{mol}{s}\right)^2 + 4\left(152.2\frac{mol}{s}\right)[1.378+0.221](0.221)\,\overset{(atm)^2\,mol/s}{1674.2}\right]^{1/2}}{2\,(152.2\,mol/s)(1.378+0.221)\,atm}$$

$X = 0.723$

∴ presence of steam increases conversion

$$K_p = \frac{F_S F_{H_2}}{F_{EB}} \frac{P}{F_T}$$

① if K_p = constant, then increasing F_T will result in an increase in F_S & F_{H_2} and X increases

② increase P will cause X to decrease

Equilibrium Calculations

Stoic Table

EB	F_{EB_0}	$-F_{EB_0}X$	$F_{EB} = F_{EB_0}(1-X)$
S	0	$+F_{EB_0}X$	$F_S = F_H = F_{EB_0}X$
H	0	$+F_{EB_0}X$	$F_H = F_{EB_0}X$
W	F_{W_0}	0	F_{W_0}

$$p_i = \frac{F_i}{F_T}P \qquad F_T = F_{EB_0} + F_{W_0} + F_{EB_0}X$$

$$k_p = \frac{F_{EB_0}X_{EB}^2 P}{F_T(1-X_{EB})} = \frac{F_{EB_0}X^2 P}{(F_{T_0} + F_{EB_0}X)(1-X)}$$

$$(k_p F_{T_0} + k_p F_{EB_0}X)(1-X) = F_{EB_0}X^2 P$$

$$k_p F_{T_0} + k_p F_{EB_0}X - k_p F_{T_0}X - k_p F_{EB_0}X^2 = F_{EB_0}X^2 P$$

$$X^2(F_{EB_0}P + k_p F_{EB_0}) + X(\overbrace{k_p F_{T_0} - k_p F_{EB_0}}^{k_p F_{W_0}}) - k_p F_{T_0} = 0$$

$$\frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \text{where} \quad ax^2 + bx + c = 0$$

$$X = \frac{-k_p(F_{W_0}) \pm \sqrt{(k_p F_{W_0})^2 + 4F_{EB_0}(P + k_p)k_p F_{T_0}}}{2F_{EB_0}(P + k_p)}$$

References:

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[1] Hermann, Ch.; Quicker, P.; Dittmeyer, R., "Mathematical simulation of catalytic dehydrogenation of ethylbenzene to styrene in a composite palladium membrane reactor." J. Membr. Sci. (1997), 136(1-2), 161-172.

[2] Fogler, H. S. *Elements of Chemical Reaction Engineering*, 3rd Ed., by, Prentice Hall PTR, Englewood Cliffs, NJ (1999).