Chemical Engineering Thermodynamics

CHEMICAL REACTION EQUILIBRIUM

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Outcomes for This Chapter

a) To define what is extend of reaction and relate it to the mole fraction (composition)

b) To derive the equilibrium criteria for chemical reaction

c) Use b) to derive equilibrium constant (K) and able to calculate K

d) To relate K to fugacity and mole fraction and able to calculate the equilibrium conversion for gas phase reaction

e) Analyze the effect of T and P on K and equilibrium composition endothermic and exothermic reactions

Commercial Chemical-Reaction

1. Chemical reaction is the heart of chemical processes.

2. Take place in a reactor.

3. A value-added process.

   Transform raw materials into products of greater value.

   Economic potential or Gross Profit must be positive.
   i.e. Main products have a higher price than
   the raw materials (reactants).

   Gross Profit is based solely on price of reactants and products , excluding the equipment and operating costs.

Study of Chemical-Reaction

1. Reaction Kinetics

   The study of rates of reaction
   i.e. How fast is the reaction?
   You will learn this in your Chemical Reaction Engineering class.

2. Chemical Reaction Equilibrium

   Determination of maximum possible conversion in a chemical reaction.
   This chapter will cover this part.

Reaction Kinetics vs Conversion

1. Both reaction kinetics and equilibrium conversion are function of T, P and composition

2. Example: Exothermic reaction,

   An increase in reaction T

   will increase in rates of reaction

   but decreases the conversion.

3. So both kinetics and equilibrium conversion must be considered for optimum reactor design.

Note:

Overall Conversion

$$= \frac{\text{reactant input to process} - \text{reactant output from process}}{\text{reactant input to process}} x100$$

Single-Pass Conversion

$$= \frac{\text{reactant input to reactor} - \text{reactant output from reactor}}{\text{reactant input to reactor}} x100$$

Irreversible Reactions

Single direction (from reactants to products).
i.e. forward reaction only.

These reactions highly favor formation of the products.

$$L + R \longrightarrow P + S$$

Only an extremely small quantity of limiting reactants (if any) remains in the system at equilibrium.

Usually 100% single-pass conversion (of limiting reactant) is considered.

Reversible Reactions

Forward and reverse reactions.

Eventually equilibrium is reached where rate of forward reaction is equal to rate of reverse reaction

$$A + B \rightleftarrows C + D$$

Appreciable quantities of all reactants and products species can coexist at equilibrium.

Hence the extent of reaction (also conversion) is limited by the chemical equilibrium.

Stoichiometric Equation

$$|v_1|A_1+|v_2|A_2 \rightarrow |v_3|A_3+|v_4|A_4$$

v_1,v_2 are stoic. coefficients of reactant (- value)

v_3,v_4 are stoic. coefficients of product (+ value)

A_1, A_2, A_3, A_4 are molecules or atoms

Example,

$$\mathrm{CH}_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$v_{\mathrm{CH4}} = -1, \quad v_{\mathrm{O2}} = -2$$

$$v_{\mathrm{CO2}} = 1, \quad v_{\mathrm{H2O}} = 2$$

Reaction Coordinate (ε)

For a reaction, the changes in the number of moles (n_i) of the species present in the reaction chamber are in direct proportion to the stoichiometric numbers (v_i).

$$\frac{dn_1}{v_1} = \frac{dn_2}{v_2} = \frac{dn_3}{v_3} = \frac{dn_4}{v_4} = \frac{dn_i}{v_i} = d\varepsilon$$

$$dn_i = v_i d\varepsilon \qquad .....(13.3)$$

Example

The following reaction consumes 10 mols of methane,

$$\mathrm{CH}_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$d\varepsilon = \frac{dn_{CH4}}{\nu_{CH4}} = \frac{-10}{-1} = 10, \qquad \frac{dn_{O2}}{\nu_{O2}} = \frac{-20}{-2} = 10,$$

$$= \frac{dn_{CO2}}{\nu_{CO2}} = \frac{10}{1} = 10, \qquad \frac{dn_{H2O}}{\nu_{H2O}} = \frac{20}{2} = 10$$

Reaction coordinate (ε) characterizes the extent or degree to which a reaction has taken place.

Also known as,

the extent of reaction (as used in Felder and Rousseau),
progress variable,
degree of advancement,
degree of reaction.

For Single Reaction

For species i, integrate eqn 13.3 from initial state (ε=0) to a state where ε = ε , so

$$\int_{n_{io}}^{n_i} dn_i = \int_0^{\varepsilon} \nu_i d\varepsilon$$

$$n_i - n_{io} = \nu_i(\varepsilon - 0)$$

$$n_i = n_{io} + \nu_i \varepsilon$$

Note: At initial state prior to reaction, ε = 0

Summation over all species,

$$\sum n_i = n = \sum n_{io} + \varepsilon \sum \nu_i$$

$$= n_o + \nu\varepsilon$$

So mole fraction of species i,

$$y_i \text{ or } x_i = \frac{n_i}{n} = \frac{n_{io} + \nu_i \varepsilon}{n_o + \nu \varepsilon}$$

.... mole fraction of species i is a function of ε

Example

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

Initial composition (prior to rxn):

2 mol CH_4, 1 mol H_2O, 1 mol CO and 4 mol H_2.

Express y_i as functions of ε.

$$y_i = \frac{n_{io} + \nu_i \varepsilon}{n_o + \nu \varepsilon}$$

$$n_o = \sum n_{io} = 2 + 1 + 1 + 4 = 8$$

$$\nu = \sum \nu_i = 1 + 3 - 1 - 1 = 2$$

$$y_{CH4} = \frac{2 - \varepsilon}{8 + 2\varepsilon} \qquad y_{H2O} = \frac{1 - \varepsilon}{8 + 2\varepsilon} \qquad y_{CO} = \frac{1 + \varepsilon}{8 + 2\varepsilon} \qquad y_{H2} = \frac{4 + 3\varepsilon}{8 + 2\varepsilon}$$

For Multiple Reactions

$$dn_i = \sum_j \nu_{ij} d\varepsilon_j$$

For species i and reaction j, we integrate from initial state (ε=0) to a state where $\varepsilon_j = \varepsilon_j$, so

$$n_i - n_{io} = \sum_j \nu_{ij}(\varepsilon_j - 0)$$

$$n_i = n_{io} + \sum_j \nu_{ij}\varepsilon_j$$

Summation over all species (*i*),

$$\sum_i n_i = n = \sum_i n_{io} + \sum_i \sum_j \nu_{ij}\varepsilon_j$$

So mole fraction of species i,

$$y_i \text{ or } x_i = \frac{n_i}{n} = \frac{n_{io} + \sum_j \nu_{ij}\varepsilon_j}{\sum_i n_{io} + \sum_i \sum_j \nu_{ij}\varepsilon_j}$$

Example of multiple rxns,

Main reaction,

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Side reactions,

$$C_2H_6 + H_2 \rightarrow 2CH_4$$

$$C_2H_4 + C_2H_6 \rightarrow C_3H_6 + CH_4$$

Also for multiple reactions,

Yield

$$= \frac{\text{moles of desired product formed}}{\text{moles that would have been formed if there were no side reactions and the limiting reactant had reacted completely}}$$

Selectivity

$$= \frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}}$$

Criteria of Chem Rxn Equilibrium

From FPR for homogenous system of variable composition,

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i \qquad (11.2)$$

For system with single chemical reaction,
substitute eqn 13.3,

$$d(nG) = (nV)dP - (nS)dT + \sum_i \nu_i \mu_i d\varepsilon$$

Apply the criterion of exactness,

$$\left[\frac{d(nG)}{d\varepsilon}\right]_{T,P} = \sum_i \nu_i \mu_i$$

Using 1st law, 2nd Law and FPR, we could show that at equilibrium (see chapter 14 and next slide),

$$(dnG)_{T,P} = 0 \qquad (14.68)$$

So, at chemical rxn equilibrium,

$$\left[\frac{d(nG)}{d\varepsilon}\right]_{T,P} = 0$$

Hence,

$$\sum_i \nu_i \mu_i = 0 \qquad (13.8)$$

This is the criteria of Chemical Rxn Equilibrium

All irreversible process occurring at constant T & P proceed in such a direction as to cause a decrease in the Gibbs energy of the system.

As derived previously (eqn 11.8, 11.46),

$$d\mu_i = d\bar{G}_i = RTd\ln\hat{f}_i \qquad \text{(contant T)}$$

Integrate from standard state of pure species i
to a state of species i in a solution (at equilibrium T),

$$\mu_i - G_i^o = RT\ln\frac{\hat{f}_i}{f_i^o} \qquad \text{(contant T)}$$

$$\mu_i = G_i^o + RT\ln\frac{\hat{f}_i}{f_i^o}$$

Substitute into the criteria of chem rxn equilibrium (eqn 13.8),

$$\sum_i v_i\mu_i = \sum_i v_i(G_i^o + RT\ln\frac{\hat{f}_i}{f_i^o}) = \sum_i v_i G_i^o + RT\sum_i \ln\left(\frac{\hat{f}_i}{f_i^o}\right)^{v_i} = 0$$

Rearrange:

$$\sum_i \nu_i G_i^o + RT\sum_i \ln\left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = \sum_i \nu_i G_i^o + RT\ln\prod_i\left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = 0$$

$\prod_i$ signifies the product over all species i.

$$e.g. \qquad \prod_{i=5} a_i = a_1 a_2 a_3 a_4 a_5 .$$

Let $$\prod_i\left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = K \qquad (13.10)$$

K is known as equilibrium constant.

So,

$$\sum_i v_i G_i^o + RT \ln K = 0$$

$$\ln K = \frac{-\sum_i v_i G_i^o}{RT} = \frac{-\Delta G^o}{RT}$$

$$where,$$

$$\sum_i v_i G_i^o = \Delta G^o \qquad (13.12)$$

$$= \text{The Std Gibbs Energy Change of Rxn at equi T}$$

The data for G_i^o is available in the form of $\Delta G^o_{f,i,298}$

See Table C.4 pg 686

EXAMPLE

$$CH_4 + H_2O(g) \rightarrow CO + 3H_2$$

Calculate ΔG^o at 298K,

$$\Delta G^o = \sum_i v_i G_i^o$$

$$= v_{H2} G^o_{H2} + v_{CO} G^o_{CO} + v_{CH4} G^o_{CH4} + v_{H2O} G^o_{H2O}$$

$$= v_{H2} \Delta G^o_{f,H2,298} + v_{CO} \Delta G^o_{f,CO,298} + v_{CH4} \Delta G^o_{f,CH4,298} + v_{H2O} \Delta G^o_{f,H2O,298}$$

$$=3(0) + 1(-137169) + (-1)(-50460) + (-1)(-228572)$$

$=141863$ Joules/mol CH_4 reacted #

$$\ln K = \frac{-\Delta G^o}{RT} \qquad (13.11b)$$

$$K = \exp\left(\frac{-\Delta G^o}{RT}\right) \qquad (13.11a)$$

for $T = T_o$

$$K_o = \exp\left(\frac{-\Delta G_o^o}{RT_o}\right) \qquad (13.21)$$

Note: Data for standard state is usually available at T_0=298.15K or 25^{o}C and P^o=1 bar

Effect of T on K

To calculate *K* at T other than the standard state T of 298K. Let's use van Hoff's eqn,

$$d \ln K = \frac{\Delta H^o}{RT^2} dT \qquad (13.14)$$

If ΔH^o (std heat of rxn) could be assumed CONSTANT, integration gives,

$$\ln \frac{K}{K'} = -\frac{\Delta H^o}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) \qquad (13.15)$$

We could rearrange,

$$K = K' \exp\left[-\frac{\Delta H^o}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)\right]$$

Let's use $\Delta H^o = \Delta H_0^o$ and $T' = T_o$

$$K = K_0 \exp\left[-\frac{\Delta H_0^o}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] = K_0 \exp\left[\frac{\Delta H_0^o}{RT_0}\left(1 - \frac{T_0}{T}\right)\right]$$

$$= K_0 K_1$$

where,

$$K_1 = \exp\left(\frac{\Delta H_0^o}{RT_0}\left(1 - \frac{T_0}{T}\right)\right) \qquad (13.22)$$

$$\ln\frac{K}{K'} = -\frac{\Delta H^o}{R}\left(\frac{1}{T}-\frac{1}{T'}\right)$$

Eqn (13.15) can also be written as,

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \left(\frac{\Delta H^o}{R}\frac{1}{T'} + \ln K'\right) \qquad (13.15a)$$

Plot of $\ln K$ vs $\frac{1}{T}$ is a straightline as shown in Figure 13.2.

$$-\frac{\Delta H^o}{R} = slope$$

Exothermic reaction, slope positive,
(K decrease with increasing T)

Endothermic reaction, slope negative,
(K increase with increasing T)

If ΔH^o could not be assumed constant,

$$K = K_0 K_1 K_2$$

Note: Data for standard state is usually available at T_0=298.15K or 25^{o}C and P^o=1 bar

where,

$$K_0 = \exp\left(\frac{-\Delta G_0^o}{RT_0}\right) \qquad K_1 = \exp\left(\frac{\Delta H_0^o}{RT_0}\left(1 - \frac{T_0}{T}\right)\right)$$

$$K_2 = \exp\left\{\begin{array}{l} \Delta A[\ln\tau - (\frac{\tau - 1}{\tau})] + \frac{1}{2}\Delta B T_0 \frac{(\tau-1)^2}{\tau} + \\ \qquad \frac{1}{6}\Delta C T_0^2 \frac{(\tau-1)^2(\tau+2)}{\tau} + \frac{1}{2}\frac{\Delta D}{T_0^2}\frac{(\tau-1)^2}{\tau^2} \end{array}\right\} \qquad (13.24)$$

where, $\tau = \frac{\mathrm{T}}{\mathrm{T}_0}$ For heat capacity constant, $\Delta A = \sum_i \nu_i A_i$ etc.

Relation of *K* to equilibrium composition (y_i)

Gas-Phase Reactions.

From definition of *K*,

$$K = \prod_i \left(\frac{\hat{f}_i}{f_i^o} \right)^{\nu_i}$$

Let the standard state be the ideal-gas state of pure species *i* at P^o (= 1 bar).

$$K = \prod_i \left(\frac{\hat{f}_i}{P^o} \right)^{\nu_i} = \prod_i \left(\frac{\hat{\phi}_i y_i P}{P^o} \right)^{\nu_i} = \left(\frac{P}{P^o} \right)^{\sum \nu_i} \prod_i \left(\hat{\phi}_i y_i \right)^{\nu_i}$$

also $\sum v_i = v$

$$K = \left(\frac{P}{P^o}\right)^{v} \prod_i \left(\hat{\phi}_i y_i\right)^{v_i}$$

so

$$\prod_i \left(\hat{\phi}_i y_i\right)^{v_i} = \left(\frac{P}{P^o}\right)^{-v} K \qquad (13.26)$$

If the mixture is an ideal mixture,

$$\prod_i \left(y_i \phi_i\right)^{\nu_i} = \left(\frac{P}{P^o}\right)^{-\nu} K \qquad (13.27)$$

If the mixture is an ideal mixture at low pressure, it becomes an ideal-gas mixture, so

$$\prod_i \left(y_i\right)^{\nu_i} = \left(\frac{P}{P^o}\right)^{-\nu} K \qquad (13.28)$$

Remember, we can express y_i in terms of ε,

For single rxn,

$$y_i = \frac{n_{io} + \varepsilon \nu_i}{\sum n_{io} + \varepsilon \sum \nu_i}$$

For multiple rxns,

$$y_i = \frac{n_{io} + \sum_j \nu_{ij} \varepsilon_j}{\sum_i n_{io} + \sum_i \sum_j \nu_{ij} \varepsilon_j}$$

Effect of T and P on Equilibrium Conversion

Consider an ideal gas reaction,

$$\prod_i \left(y_i\right)^{\nu_i} = \left(\frac{P}{P^o}\right)^{-\nu} K \qquad (13.28)$$

And eqn 13.15a gives the relation of *K* wrt. *T*,

$$\ln K = -\frac{\Delta H^o}{R}\frac{1}{T} + \left(\frac{\Delta H^o}{R}\frac{1}{T'} + \ln K'\right)$$

Effect of TEMPERATURE

$$\prod_i (y_i)^{\nu_i} = \left(\frac{P}{P^o}\right)^{-\nu} K$$

For endothermic rxn, an increase in T will result in an increase in K, therefore an increase in,

$$\prod_i (y_i)^{\nu_i} = \frac{y_c^{\nu_c} y_d^{\nu_d}}{y_a^{|\nu_a|} y_b^{|\nu_b|}} \quad \uparrow$$

The composition or fraction of products will be higher.

An increase in ε_e.

Shift of rxn to the right.

Higher equilibrium conversion.

Effect of TEMPERATURE

$$\prod_i (y_i)^{v_i} = \left(\frac{P}{P^o}\right)^{-v} K$$

For exothermic rxn, an increase in T will result in a decrease in K, therefore a decrease in,

$$\prod_i (y_i)^{v_i} = \frac{y_c^{v_c} y_d^{v_d}}{y_a^{|v_a|} y_b^{|v_b|}} \downarrow$$

The composition or fraction of products will be reduced.

A decrease in ε_e.

Shift of rxn to the left.

Lower equilibrium conversion.

Effect of PRESSURE

$$\prod_i (y_i)^{\nu_i} = \left(\frac{P}{P^o}\right)^{-\nu} K$$

If *v* is negative* value, an increase in P (at constant T) causes an increase in,

$$\prod_i (y_i)^{\nu_i} = \frac{y_c^{V_c}\, y_d^{V_d}}{y_a^{|V_a|}\, y_b^{|V_b|}} \uparrow$$

The composition or fraction of products will be higher.

An increase in ε_{e}.

Shift of rxn to the right.

Higher equilibrium conversion.

*reduction in mole number

Effect of PRESSURE

$$\prod_i (y_i)^{v_i} = \left(\frac{P}{P^o}\right)^{-v} K$$

If *v* is positive* value, an increase in P (at constant T) will result in a decrease in,

$$\prod_i (y_i)^{v_i} = \frac{y_c^{V_c} y_d^{V_d}}{y_a^{|V_a|} y_b^{|V_b|}} \quad \downarrow$$

The composition or fraction of products will be reduced.

A decrease in $\varepsilon_{e.}$

Shift of rxn to the left.

Lower equilibrium conversion.
*increase in mole number

Relation of *K* to equilibrium composition (x_i)

Liquid-Phase Reactions.

From definition of *K*,

$$K = \prod_i \left(\frac{\hat{f}_i}{f_i^o} \right)^{\nu_i}$$

Let the std state be the pure liquid of species *i* at the system temperature and 1 bar. Substitute eqn 11.90,

$$K = \prod_i \left(\frac{\gamma_i x_i f_i}{f_i^o} \right)^{\nu_i}$$

To find $\frac{f_i}{f_i^o}$ in term of measured variable,

$$G_i = \Gamma_i(T) + RT\ln f_i \qquad (11.31)$$

Apply at T and std state pressure of P=1 bar,

$$G_i^o = \Gamma_i(T) + RT\ln f_i^o$$

The difference,

$$G_i - G_i^o = RT\ln\frac{f_i}{f_i^o}$$

From FPR, $dG = VdP - \cancel{SdT}$ at constant T

Integrate at constant T for pure liquid i from P^o to P,

$$G_i - G_i^o = \int_{P^o}^{P} V_i \, dP$$

Combine ,

$$RT \ln \frac{f_i}{f_i^o} = \int_{P^o}^{P} V_i \, dP$$

For $V_i = V_i^{liq} \approx$ constant

$$RT \ln \frac{f_i}{f_i^o} = V_i (P - P^o)$$

So,

$$\ln\frac{f_i}{f_i^o}=\frac{V_i(P-P^o)}{RT} \qquad \frac{f_i}{f_i^o}=\exp\left(\frac{V_i(P-P^o)}{RT}\right)$$

Substitute and rearrange,

$$K=\prod_i\left(\frac{\gamma_i x_i f_i}{f_i^o}\right)^{v_i}=\prod_i\left(\gamma_i x_i \exp\left(\frac{V_i(P-P^o)}{RT}\right)\right)^{v_i}$$

$$=\prod_i(\gamma_i x_i)^{v_i}\exp\left(\frac{v_i V_i(P-P^o)}{RT}\right)=\exp\left(\frac{(P-P^o)}{RT}\sum_i(v_i V_i)\right)\prod_i(\gamma_i x_i)^{v_i}$$

So,

$$\prod_i(\gamma_i x_i)^{v_i}=K\exp\left(\frac{(P^0-P)}{RT}\sum_i(v_i V_i)\right) \qquad (13.31)$$

The exponent term is usually 1, except for high pressure system, so,

$$\prod_i (\gamma_i x_i)^{\nu_i} = K \qquad (13.32)$$

For ideal liquid solution,

$$\prod_i (x_i)^{\nu_i} = K \qquad (13.33)$$ Known as the law of mass action

As shown earlier, x_i can be written in term of ε

Exercise

- Calculate K in Example 13.5a and for equilibrium reaction, determine the fractional conversion of steam.

- Fractional conversion of steam

  = ε / (initial mol of steam)

Thank You