

Chemical Reaction Engineering - Part 5

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Reversible reactions

All chemical reactions are reversible. Many times in this course we keep things simple by considering reactions under conditions where the reactant conversion at equilibrium is almost complete. We call those reactions "essentially irreversible" or even "irreversible." But we always remember that this is short-hand talk and that all reactions are reversible.

Now we consider both the forward and back (reverse) reactions for components in a single stoichiometric equation. We say "back" and use subscript "b" rather than "reverse" because we already use subscript "r" for reaction.

Consider this reaction of liquids, $A = B$. In reality, this would be an isomerization reaction, since there are only two components involved. Different isomers of the same compound are different components in reaction rate and in thermodynamic equations.

Specify that the rate of generation of component A is the following

$$r_A = -k_f C_A + k_b C_B$$

Remember from stoichiometry that

$$\frac{r_i}{\nu_i} = \frac{r_j}{\nu_j} = \frac{r_k}{\nu_k} = \text{constant for all components in one reaction}$$

Therefore,

$$\frac{r_A}{\nu_A} = \frac{r_B}{\nu_B} = \text{constant} = \frac{r_A}{-1} = \frac{r_B}{+1}$$

$$r_B = -r_A = k_f C_A - k_b C_B$$

This relationship is obvious for this simple case but it will be useful for reactions with more complex stoichiometric equations.

If we start with pure A and then B starts to be formed, then A is obviously the reactant. What if we were to start with pure B and then A starts to be formed? Then we would swap the stoichiometric equation left to right ($B = A$) and B would become the reactant with formal stoichiometric coefficient = -1 and A would become the product.

At equilibrium, the net rate of generation of all components in a reaction is zero. We say "net" because the reactions don't stop but the forward rate equals the back rate at equilibrium so the net rate is zero.

$$r_A = -k_f C_A + k_b C_B = 0 \text{ at equilibrium}$$

$k_f C_A = k_b C_B$ at equilibrium

$$\frac{k_f}{k_b} = \frac{C_B}{C_A}$$

We know from our thermo course that a reaction equilibrium constant in terms of concentration K_c is equal to the product of the component concentrations, each raised to the power of its formal stoichiometric coefficient.

$$K_c = \frac{C_B}{C_A}$$

Therefore,

$$K_c = \frac{k_f}{k_b}$$

The dimensions of K_c are the dimensions of concentration raised to a power equal to the sum of the formal stoichiometric coefficients.

For gases and rate equations in terms of gas pressures, the dimensions of the equilibrium constant in terms of pressure K_p has dimensions of pressure raised to a power equal to the sum of the formal stoichiometric coefficients.

In a section below, we show how K_c and K_p are related to the formal thermodynamic equilibrium constant K_{eq} and how to compute the value of K_{eq} .

Component balance

For this reaction in a batch reactor, the component balance on A is

$$\frac{dN_A}{dt} = r_A V = (-k_f C_A + k_b C_B) V$$

In some problems we may be given the forward rate equation but not the back rate equation and asked a question about conversion vs. time. We can derive a back rate equation that is consistent with equilibrium by making sure that the ratio of the concentration terms of the back and forward rate equations are consistent with the thermodynamic equilibrium relationship. For example,

$$\frac{dN_A}{dt} = -k_f (C_A - C_B / K_{eq,c}) V$$

For a constant volume batch reactor, we get

$$\frac{dC_A}{dt} = -k_f C_A + k_b C_B$$

We seem to have a problem. We appear to have two dependent variables (C_A and C_B) but only one ODE. The solution is to write a stoichiometric table.

$$N_A = N_{A,0} - N_{A,0} X_A$$

$$N_B = N_{B,0} + N_{A,0} X_A$$

$$N_{tot} = N_{tot,0}$$

We remember that $C_i = N_i/V$ for batch reactors and we can substitute that relationship into the balance equation. Since we have constant volume, we can take a short cut and write the table this way.

$$C_A = C_{A,0} - C_{A,0} X_A$$

$$C_B = C_{B,0} + C_{A,0} X_A \quad \text{for constant Volume only (be careful with short cuts!)}$$

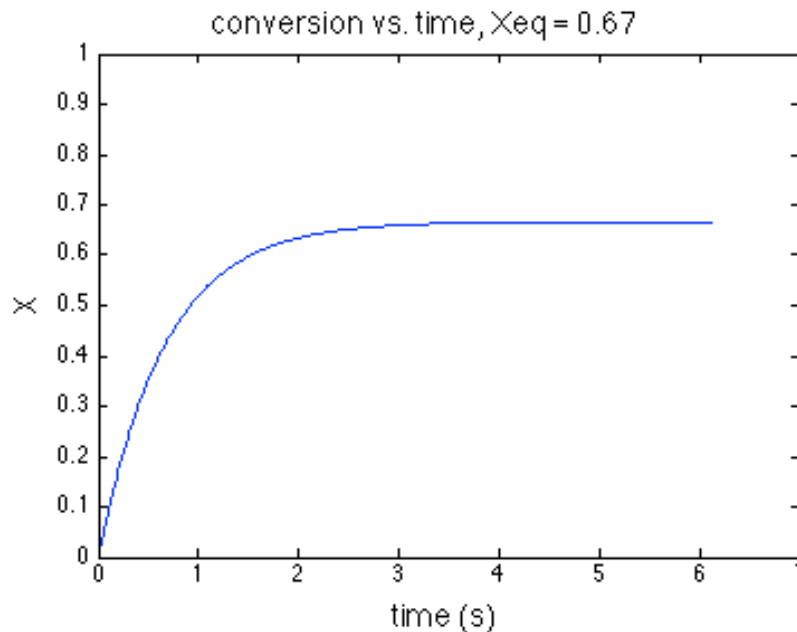
$$C_{tot} = C_{tot,0}$$

Substituting into our balance equation, we now have one dependent variable (X_A) for one ODE.

$$\frac{dX_A}{dt} = k_f(1 - X_A) - k_b((C_{B,0}/C_{A,0}) + X_A)$$

If we want to know how the conversion changes with time, then we would integrate this equation.

For example, for $C_{A0} = 1 \text{ mol/m}^3$, $C_{B0} = 0$, $k_f = 1 \text{ s}^{-1}$, $k_b = 0.5 \text{ s}^{-1}$,



This ODE is separable and has an analytical solution but I used Euler's method in Matlab to illustrate using a loop convergence criterion.

```
% integrate to equilibrium in isothermal batch reactor
% A = B
% rA = -kf*CA + kb*CB
CA0 = 1; % mol/m3, initial concentration of A
CB0 = 0; % mol/m3, initial concentration of B
kf = 1; % (1/s), forward rate coefficient
kb = 0.5; % (1/s), back rate coefficient
% this has an analytical solution
% but will do Euler's to illustrate loop convergence criterion
i = 1;
t(1) = 0; % s, time
x(1) = 0; % conversion
cc = 1e-6 % convergence criterion
ccCheck = 1; % to enter loop first time
dt = 0.01; % s, time step (could estimate from k's)
while ccCheck >= cc
    dxdt = kf*(1-x(i))-kb*(CB0/CA0+x(i)); % variable dxdt = dx/dt (not dx*dt)
    x(i+1) = x(i) + dxdt * dt;
    t(i+1) = t(i) + dt;
    ccCheck = abs(x(i+1)-x(i));
    i = i+1;
end
plot(t,x)
tt = sprintf('conversion vs. time, Xeq = %4.2f', max(x))
title(tt)
ylabel('X'), xlabel('time (s)')
axis([0 ceil(max(t)) 0 1])
```

Equilibrium conversion

At relatively long time, the conversion will approach a constant value, the "equilibrium conversion."

We can determine the equilibrium conversion by integrating the ODE by stepping in time (e.g., Euler's method) until the change in conversion from step to step is very small (exit repeat when a convergence criterion is met).

If we only want the equilibrium conversion $X_{A,eq}$ we don't have to integrate. At equilibrium, $dX_A/dt = 0$

$$k_f(1 - X_A) = k_b((C_{B,0}/C_{A,0}) + X_A)$$

$$K_c = \frac{k_f}{k_b} = \frac{((C_{B,0}/C_{A,0}) + X_{A,eq})}{(1 - X_{A,eq})}$$

Since equilibrium is a thermodynamic state property, knowing K_c we can solve for $X_{A,eq}$ without having to know the forward and back rate equations.

$$K_c = \frac{C_B}{C_A} = \frac{((C_{B,0}/C_{A,0}) + X_{A,eq})}{(1 - X_{A,eq})}$$

In favorable cases we can get the value of K_c from the Gibbs free energy change of the reaction as shown in the section below

Thermodynamic definition of equilibrium constant

Here we consider reactions in a single phase and give a general overview. The objective is to show that the K_c we use to compute equilibrium compositions is related to the Gibbs free energies of the reaction components and not just a constant that appears out of nowhere. Consult your thermo text for details.

The formal thermodynamic equilibrium constant K_{eq} is defined in relation to the standard Gibbs free energy change of the reaction $\Delta_r G^0$ at specified conditions.

$$\Delta_r G^0 = -RT \ln(K_{eq}) \quad \text{at reaction temperature } T$$

$$\Delta_r G^0 = \sum \nu_i \bar{G}_i^0$$

where \bar{G}_i^0 is the partial molar Gibbs free energy of component i and ν_i is the formal stoichiometric coefficient of component i . For pure components and components in ideal mixtures, the partial molar Gibbs free energy of i equals the Gibbs free energy of formation of i , $\bar{G}_i^0 = \Delta_f G_i^0$. The dimensions of $\Delta_r G^0$ are energy per mole extent of reaction.

K_{eq} is equal to the product of the activities of each component raised to the power of its formal stoichiometric coefficient.

$$K_{eq} = \prod a_i^{\nu_i}$$

where a_i is the chemical activity of component i in a mixture at reaction conditions relative to component i at specified standard state conditions. Activity is dimensionless and K_{eq} is dimensionless.

The numerical values of the dimensionless activities a_i and, thus, the numerical value of K_{eq} are dependent on the standard state conditions specified.

Specification of standard state conditions is relatively straightforward for mixtures of gases. Usually the standard state pressure is specified to be 1 atm or 1 bar.

Specification of standard state conditions is more complex for liquid mixtures. This is because there are a variety of different types of liquid mixtures: solutions of electrolytes vs. non electrolytes, dilute vs. concentrated, etc.

We will consider only one type of liquid mixture here: a dilute solution of non electrolyte reactants in a solvent. Henry's Law is assumed to hold.

$$a_i = \frac{\gamma_{ic}^H C_i}{C_\theta} \quad \text{for dilute solution of non electrolytes}$$

where γ_{ic}^H is the Henry's activity coefficient of component i and C_θ is a specified standard state concentration. Values of C_θ of 1 mol/liter (1 molar) or, more commonly, 1 mol/kg (1 molal) are chosen, with the C_i having the same units as C_θ .

$$K_{eq} = \prod a_i^{v_i} = \prod \left(\frac{\gamma_{ic}^H C_i}{C_\theta} \right)^{v_i}$$

We can separate K_{eq} into three terms:

$$K_{eq} = \left(\prod C_i^{v_i} \right) \left(\prod C_\theta^{-v_i} \right) \left(\prod \gamma_{ic}^{v_i} \right)$$

$$K_{eq} = K_c K_{c\theta} K_\gamma$$

The concentration dimensions of the first two terms $K_c K_{c\theta}$ cancel each other, and the numerical value of the second term $K_{c\theta} = 1$ for standard state concentrations of 1 mol/liter or 1 mol/kg. K_γ accounts for non-ideal solution behavior.

For either choice of standard state concentration, K_{eq} will be dimensionless. However, when there is a change in total moles on reaction, K_{eq} will have a different numerical value depending on the units chosen. The standard Gibbs free energy change of the reaction $\Delta_r G^0$ must be referenced to the same specified standard state conditions as K_{eq} .

Our goal is to get a value of K_c so that we can use it to compute equilibrium concentrations. This would require getting values of $\Delta_r G^0$ and K_γ . This is sufficiently challenging for most liquid-phase reactions such that we may be more likely to find data for K_c which have been measured experimentally.

Consult your thermodynamics text for other types of liquid mixtures.

For gas mixtures, the situation is more straightforward. For gas mixtures,

$$a_i = \frac{\varphi_i}{\varphi_0}$$

where fugacity φ_i has dimensions of pressure. The standard state fugacity of gases φ_0 is usually 1 atm or 1 bar - check which is used in your source of thermodynamic data.

The fugacity of gas i is equal to the fugacity coefficient of i ϕ_i times the partial pressure of i , p_i . Fugacity coefficients are dimensionless. Fugacity coefficients show the deviation from ideal gas behavior.

$$a_i = \frac{\phi_i p_i}{\varphi_0}$$

$$K_{eq} = \prod a_i^{v_i} = \prod \left(\frac{\varphi_i}{\varphi_0} \right)^{v_i}$$

$$K_{eq} = \prod \left(\frac{\phi_i p_i}{\varphi_0} \right)^{v_i}$$

We can separate K_{eq} into three terms:

$$K_{eq} = \left(\prod p_i^{v_i} \right) \left(\prod \varphi_0^{-v_i} \right) \left(\prod \phi_i^{v_i} \right)$$

$$K_{eq} = K_p K_{\varphi_0} K_\phi \quad K_{eq} \text{ is a function of } T, \text{ and is not a function of } P$$

$$K_p = \prod p_i^{v_i} \quad \text{e.g., with units } (\text{atm})^{\sum v_i} \quad \text{and where } K_p \text{ varies with } P_{tot} \text{ with change in moles}$$

$$p_i = y_i P \quad \text{where } y_i \text{ is the mole fraction of component } i$$

$$K_{\varphi_0} = 1 \quad \text{with units } \left(\frac{1}{\text{atm}} \right)^{\sum v_i} \quad \text{when the standard state fugacity, } \phi_0 = 1 \text{ atm}$$

$$K_\phi = \prod \phi_i^{v_i} \quad \text{dimensionless, accounts for non ideal gas behavior}$$

The pressure dimensions of the first two terms $K_p K_{\varphi_0}$ cancel each other, and the numerical value of the second term $K_{\varphi_0} = 1$ for standard states of 1 atm or 1 bar. Check your source of thermodynamic data, since other standard states could be used, e.g., 101.325 kPa.

If you were to use pressure units of kPa in K_p and the standard state is 101.325 kPa, then

$$K_{\varphi_0} = \left(\frac{1}{101.325 \text{ kPa}} \right)^{\sum v_i} \quad \text{and the numerical value of } K_{\varphi_0} \neq 1 \text{ for } \sum v_i \neq 0$$

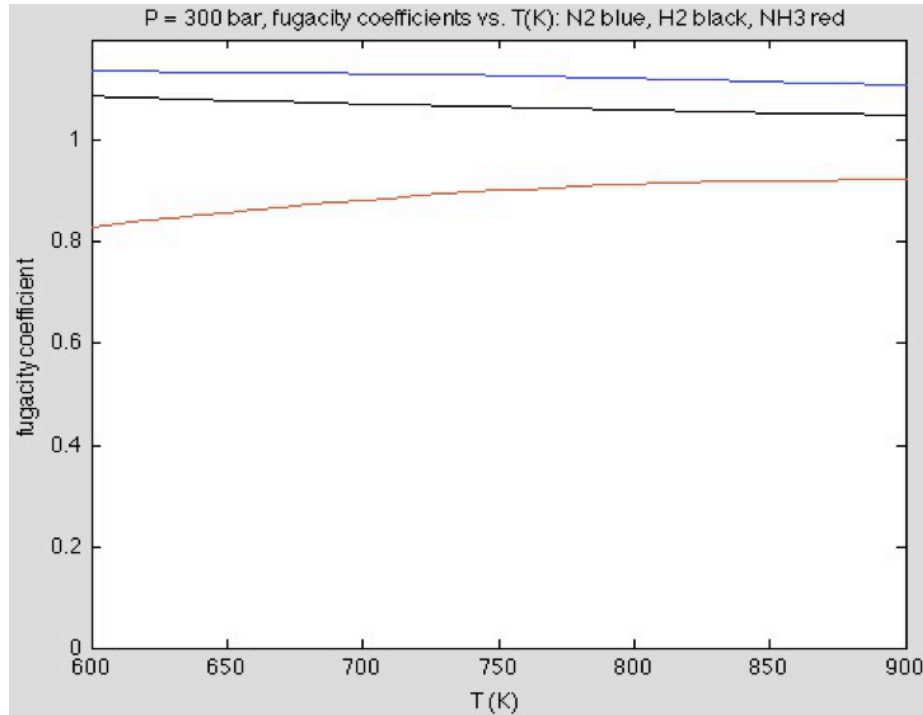
Gases near atmospheric pressure can be approximated as ideal gases, so the product of fugacity coefficients $K_\phi = 1$.

Gases at high pressure are not ideal, so the product of fugacity coefficients $K_\phi \neq 1$.

In general, fugacity coefficients are functions of mixture composition as well as temperature and pressure. In some cases, we may be able to use pure-component fugacity coefficients as an approximation.

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For example, below is a plot of fugacity coefficients at 300 bar for N₂, H₂ and NH₃ gases, which are the reactants and product in an ammonia synthesis reactor. This reaction is run at high pressure in order to obtain significant equilibrium conversion to ammonia - note the decrease in total moles with conversion to ammonia. Ammonia is used to make fertilizer. About half of the nitrogen atoms in the protein molecules in your body may have passed through an ammonia synthesis reactor.¹



The Matlab program for this plot is in CRE Notes, Part 5-A, ammonia equilibrium.

Back to computing the equilibrium coefficient from the Gibbs free energy change of the reaction.

$$\Delta_r G^0 = -RT \ln(K_{eq}) \quad \text{at reaction temperature } T$$

$$\Delta_r G^0 = \sum (v_i \Delta_f G_i^0) \quad \text{at reaction temperature } T$$

$$\Delta_r G^0 = -\Delta_f G_A^0 + \Delta_f G_B^0 \quad \text{for } A = B \text{ reaction example}$$

The standard free energies of formation $\Delta_f G_i^0$ can be found using standard reference sources. Of course, A and B here would be replaced by the real chemical components they represent in our equations.

¹Vaclav Smil, "Global population and the nitrogen cycle," Scientific American, July, pp. 76-81 (1997).

The CRC Handbook of Chemistry and Physics is available online via the UCSD Library at <http://roger.ucsd.edu/record=b2704963~S9>

The NIST-JANAF² Thermochemical Tables are on the web at <http://kinetics.nist.gov/janaf/>
Below is a screenshot for a gaseous component.

Carbon Monoxide (CO) C₁O₁(g)

Enthalpy Reference Temperature = $T_r = 298.15$ K Standard State Pressure = $p^\circ = 0.1$ MPa

T/K	J·K ⁻¹ mol ⁻¹				kJ·mol ⁻¹		
	C_p°	S°	$-(G^\circ - H^\circ(T_r))/T$	$H - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log K_f
0	0.000	0.000	INFINITE	-8.671	-113.805	-113.805	INFINITE
100	29.104	165.850	223.539	-5.769	-112.415	-120.239	62.807
200	29.108	186.025	200.317	-2.858	-111.286	-128.526	33.568

The "free energy function" is tabulated because it varies less dramatically with T than $\Delta_f G^0$ and, thus, interpolations for T's between tabulated values can be performed more accurately.

$$-\frac{G^0 - H_{298K}^0}{T} \quad \text{"free energy function"}$$

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²NIST-JANAF = National Institute of Standards and Technology - Joint Army Navy Air Force.

The NIST Chemistry WebBook is on the web at <http://webbook.nist.gov/chemistry/>

Here is a screenshot for gaseous carbon monoxide. Click the "View table" link to get a table of the "free energy function" vs. T in the NIST Chemistry WebBook.

→ ↻ 🏠 webbook.nist.gov/cgi/cbook.cgi?Name=carbon+monoxide&Units=SI&cTG=on

Gas phase thermochemistry data

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Quantity	Value	Units	Method	Reference	Comment
$\Delta_f H^\circ_{\text{gas}}$	-110.53 ± 0.17	kJ/mol	Review	Cox, Wagman, et al., 1984	CODATA Review value
$\Delta_f H^\circ_{\text{gas}}$	-110.53	kJ/mol	Review	Chase, 1998	Data last reviewed in September, 1965
Quantity	Value	Units	Method	Reference	Comment
$S^\circ_{\text{gas,1 bar}}$	197.660 ± 0.004	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value
$S^\circ_{\text{gas,1 bar}}$	197.66	J/mol*K	Review	Chase, 1998	Data last reviewed in September, 1965

Gas Phase Heat Capacity (Shomate Equation)

$$C_p^\circ = A + B*t + C*t^2 + D*t^3 + E/t^2$$

$$H^\circ - H^\circ_{298.15} = A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H$$

$$S^\circ = A*\ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G$$

C_p = heat capacity (J/mol*K)
 H° = standard enthalpy (kJ/mol)
 S° = standard entropy (J/mol*K)
 t = temperature (K) / 1000.

[View plot](#) Requires a Java capable browser.

[View table.](#)

Temperature (K)	298. - 1300.	1300. - 6000.
A	25.56759	35.15070
B	6.096130	1.300095
C	4.054656	-0.205921
D	-2.671301	0.013550
E	0.131021	-3.282780
F	-118.0089	-127.8375
G	227.3665	231.7120
H	-110.5271	-110.5271
Reference	Chase, 1998	Chase, 1998
Comment	Data last reviewed in September, 1965	Data last reviewed in September, 1965

As an alternative to using tabulated free energy function values, you can compute the Gibbs free energy change from the enthalpy and entropy equations evaluated at the reaction temperature. $\Delta G = \Delta H - T\Delta S$

In this example, in order to introduce concepts, we specify the simplest reaction (A=B) with no change in moles and with constant volume. However, prepare yourself to be able to handle more complex problems.

Don't worry. You can do that by applying the tools you have learned. The key is to work in a logical progression with the tools you are learning and not jump to conclusions!

Types of problems

Given a stoichiometric equation and a forward rate equation, be able to write back (reverse) rate equation such that the full, net rate of reaction equation is consistent with thermodynamic equilibrium. Be able to compute $\Delta_r G$ and K_{eq} given T and a list of components (real ones, not A and B). Given an initial composition (list of component moles or concentrations), be able to compute equilibrium conversion or composition. Be able to compute the change in conversion or composition vs. time from initial conditions until equilibrium is closely approached.

Important terms

Equilibrium conversion, $X_{A,eq}$

Equilibrium composition, concentrations

Equilibrium constant K_{eq} - know how to compute from $\Delta_r G$

Gibbs free energy of reaction, $\Delta_r G$ - know how to compute from $\Delta_f G_i$

Activity, activity coefficient

Fugacity, fugacity coefficient

Free energy function

Additional resources

For this subject, it's best to consult your material and energy balance textbook and your thermo textbook.