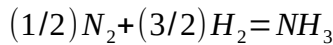


## Chemical Reaction Engineering - Part 5-A

### Reaction equilibria with change in gas moles and nonideal gas: ammonia synthesis

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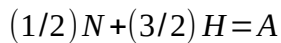
The formal thermodynamic equilibrium constant  $K_{eq}$  is defined in relation to the standard Gibbs free energy change of the reaction, where the standard Gibbs free energy change is a function of  $T$ .

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

$$K_{eq} = K_p K_{\phi_0} K_{\phi} \quad ; \quad K_p = \prod p_i^{v_i} \quad ; \quad K_{\phi_0} = \prod \varphi_0^{-v_i} \quad ; \quad K_{\phi} = \prod \phi_i^{v_i}$$

The pressure dimensions of the first two terms  $K_p K_{\phi_0}$  cancel each other, and the numerical value of the second term is one:  $K_{\phi_0} = 1$  for standard states of 1 atm or 1 bar. For ideal gases, the dimensionless fugacity coefficient product,  $K_{\phi} = 1$ .

To speed writing



$$K_p = \frac{p_A}{p_N^{1/2} p_H^{3/2}} = \frac{y_A P}{(y_N P)^{1/2} (y_H P)^{3/2}} = \frac{y_A}{y_N^{1/2} y_H^{3/2}} \left( \frac{1}{P} \right) \quad \text{for } \Delta_r G^0 \text{ per mol A}$$

$$y_i = \frac{N_i}{N_{tot}}$$

Write a stoichiometric table in terms of the conversion of  $N_2$ ,  $X_N$

For  $N + 3H = 2A$

$$N_N = N_{N0} - N_{N0} X_N$$

$$N_H = N_{H0} - 3 N_{N0} X_N$$

$$N_A = N_{A0} + 2 N_{N0} X_N$$

$$N_I = N_{I0}$$

$$N_{tot} = N_{tot,0} - 2 N_{N0} X_N$$

$$K_p = \frac{(\Theta_{A0} + 2 X_N)}{(1 - X_N)^{1/2} (\Theta_{H0} - 3 X_N)^{3/2}} \left( \frac{1}{y_{N0}} - 2 X_N \right) \left( \frac{1}{P} \right)$$

where

$$\Theta_{i0} = \frac{N_{i0}}{N_{N0}}$$

An alternative would be to write the stoichiometric table in terms of the stoichiometric extent of reaction. Using the stoichiometric extent as the variable, the stoichiometric equation could be kept in the original form as  $(1/2) N + (3/2) H = A$ , or any other valid form (multiplied by any constant).

In cases of multiple reactions and solving for equilibrium compositions, stoichiometric extents should be used as variables, since using conversions as variables becomes awkward in many cases. After extents are found, then any desired reactant conversion can be computed. Solving equilibrium equations for multiple reactions involves coupled nonlinear equations and may require special solution algorithms.

For example, for a stoichiometric feed with no ammonia nor inerts,

$$\Theta_{A0} = 0, \quad \Theta_{H0} = 3, \quad y_{N0} = 1/4$$

$$K_p = \frac{2 X_N}{(1 - X_N)^{1/2} (3 - 3 X_N)^{3/2}} (4 - 2 X_N) \left( \frac{1}{P} \right)$$

This is a quadratic equation in  $X_N$

$$(A+2) X_N^2 - (2A+4) X_N + A = 0 \quad \text{where} \quad A = P K_p \left( \frac{27}{4} \right)^{1/2} = 2.5981 P K_p$$

The fact that this is a quadratic equation is not a general result. Other reaction stoichiometry will give other equations.

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

Gases at high pressure are not ideal, and the ammonia synthesis reaction operates at high pressure, so the fugacity coefficient product,  $K_\phi \neq 1$ .

Dyson and Simon gave equations for the fugacity coefficients of the individual gases [Ind. & Eng. Fund. 7, 605 (1968) <http://pubs.acs.org/doi/pdf/10.1021/i160028a013?source=chemport&>]. Equations for the fugacity coefficients are also given in H.F. Rase, "Chemical Reactor Design for Process Plants," vol. 2 "Case Studies and Design Data," Wiley (1977), p. 64.

Gillespie and Beattie analyzed experimental data and obtained a correlation for the fugacity coefficient product  $K_\phi$  for ammonia synthesis,

$$\log_{10} \left( \frac{1}{K_\phi} \right) = P \left( \frac{0.1191849}{T} + \frac{91.87212}{T^2} + \frac{25122730}{T^4} \right)$$

where the total pressure  $P$  has units of (atm) and the standard state fugacities  $\phi_0 = 1$  atm [Phys. Rev. 36, 743 (1930) <http://dx.doi.org/10.1103/PhysRev.36.743> ].

Using the equation from Gillespie and Beattie with  $P = 300$  bar (292.6 atm) and  $T = 800$  K (523 °C),

$$K_\phi = 0.7856$$

Get the free energy change here from the free energy function tables at the NIST Chem WebBook. For example, for direct link to gas phase thermochemistry table for ammonia, go to:

<http://webbook.nist.gov/cgi/cbook.cgi?ID=C7664417&Units=SI&Mask=1&Type=JANAFG&Table=on#JANAFG>

Component	stoich. coeffic.	$-(G^\circ - H^\circ_{298})/T$ (J/mol/K) (at 800 K)	$\Delta_f H^\circ_{298}$ (kJ/mol)
NH <sub>3</sub>	+1	207.2	-45.90
H <sub>2</sub>	-3/2	141.2	0.0
N <sub>2</sub>	-1/2	202.2	0.0

$$\sum v_i (G^\circ - H^\circ_{298})_i = \Delta_r (G^\circ - H^\circ_{298}) = \Delta_r G^\circ - \Delta_r H^\circ_{298} = 84.56 \text{ kJ/mol-NH}_3 \quad \text{at 800 K}$$

$$\sum v_i (\Delta_f H^\circ_{298})_i = \Delta_r H^\circ_{298} = -45.90 \text{ kJ/mol-NH}_3$$

$$\Delta_r G^\circ = 38.66 \text{ kJ/mol-NH}_3$$

$$-\ln(K_{eq}) = \frac{\Delta_r G^\circ}{RT}$$

$$K_{eq} = 0.002991 \quad \text{at 800 K}$$

Now, we can solve for  $X_N$  at these conditions.

$$K_p = \frac{K_{eq}}{K_\phi K_\phi} = \frac{0.002991}{(1)(0.7856)} = 0.003807$$

In our quadratic equation above for a stoichiometric feed with no ammonia or inerts in feed,

$$A = 2.5981 P K_p = 2.5981(292.6)(0.003807) = 2.894$$

$$(A+2) X_N^2 - (2A+4) X_N + A = 0$$

$$4.894 X_N^2 - 9.788 X_N + 2.894 = 0$$

$$X_N = 0.361 \quad \text{at equilibrium for non-ideal gas with } K_\phi = 0.7856 \quad \text{at 300 bar, 800 K}$$

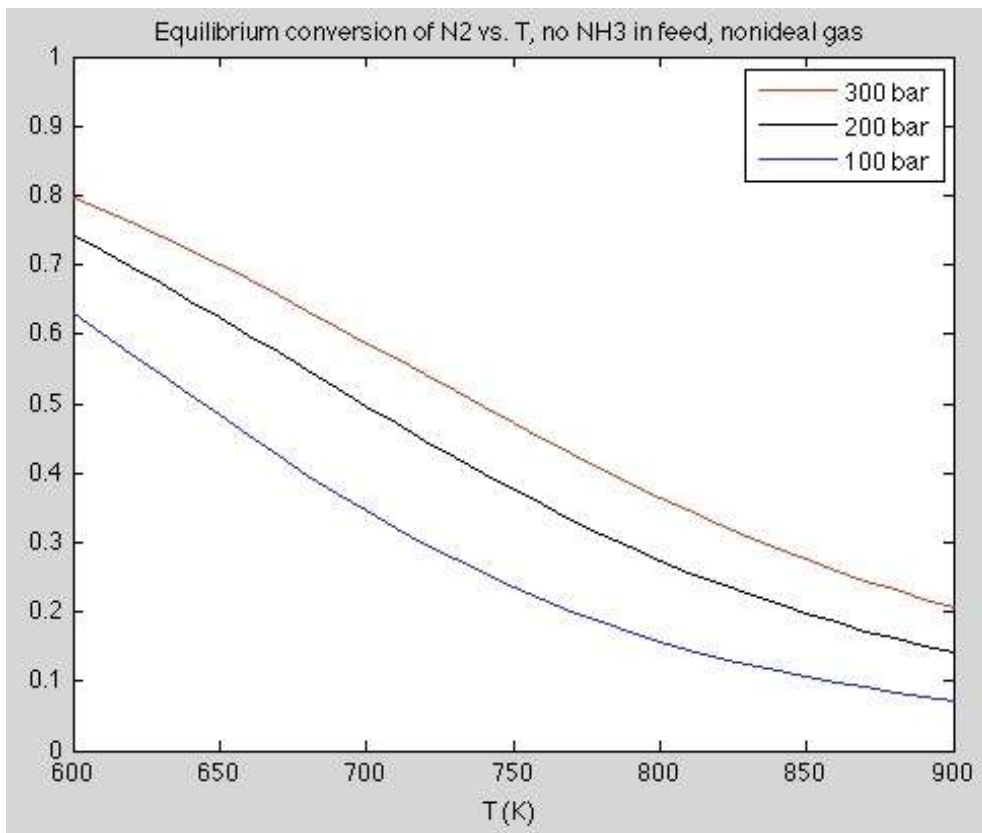
I used Matlab's roots (of polynomial) function to solve:  $a = 2.894$ ,  $\text{roots}([a+2 \quad -(2*a+4) \quad a])$ .

You could also use WolframAlpha.com: `solve (a+2)x^2 - (2a+4)x + a = 0` with  $a = 2.894$ . There are two roots. For conversion, the valid root is the one between 0 and 1.

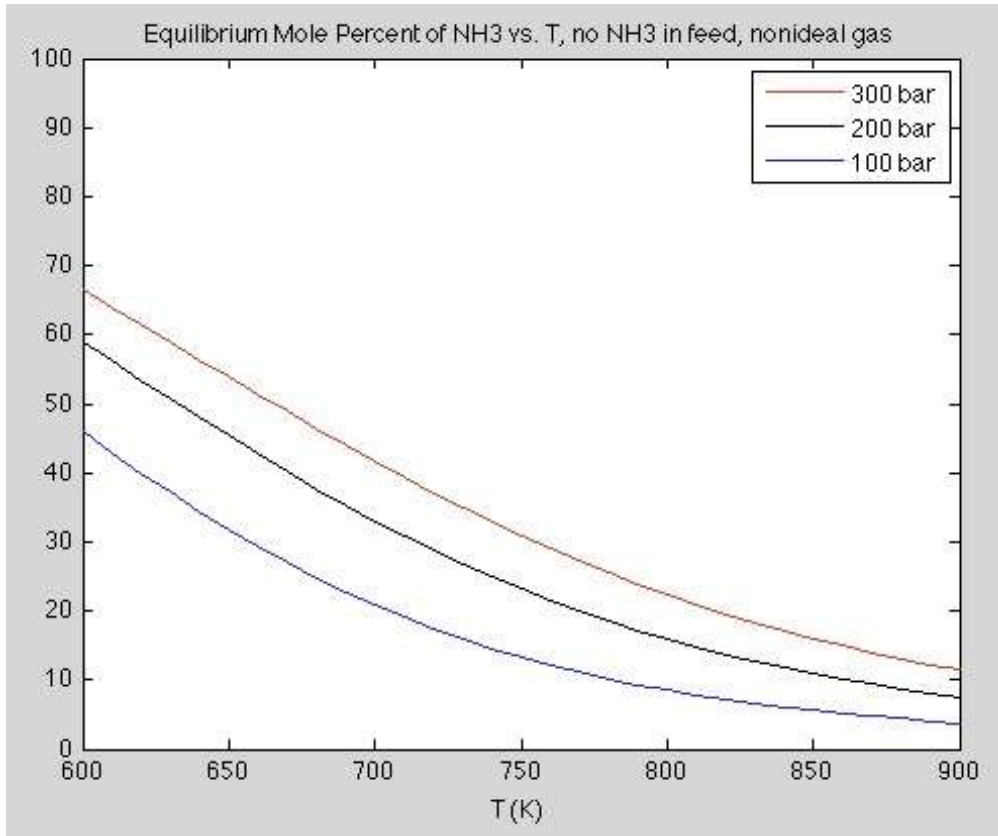
For our feed and these conditions, the ammonia mole percent at equilibrium is 22.0 mol%.

If we had assumed ideal gases with  $K_\phi = 1$  then  $X_N = 0.316$  at equilibrium with ideal gases, and the ammonia percent would be 18.8 mol% instead of 22.0 mol% - a significant difference.

The figure below shows the equilibrium conversion for a stoichiometric mixture of  $H_2$  and  $N_2$  with no  $NH_3$  in the feed. Non-ideal gas behavior was used. The "good news" is that the equilibrium conversion is high at low temperature. The "bad news" is that the reaction is slow at low temperatures so the amount of catalyst needed is high. In all cases, the equilibrium conversion is low such that you need to separate and recycle reactants. A nice design problem!



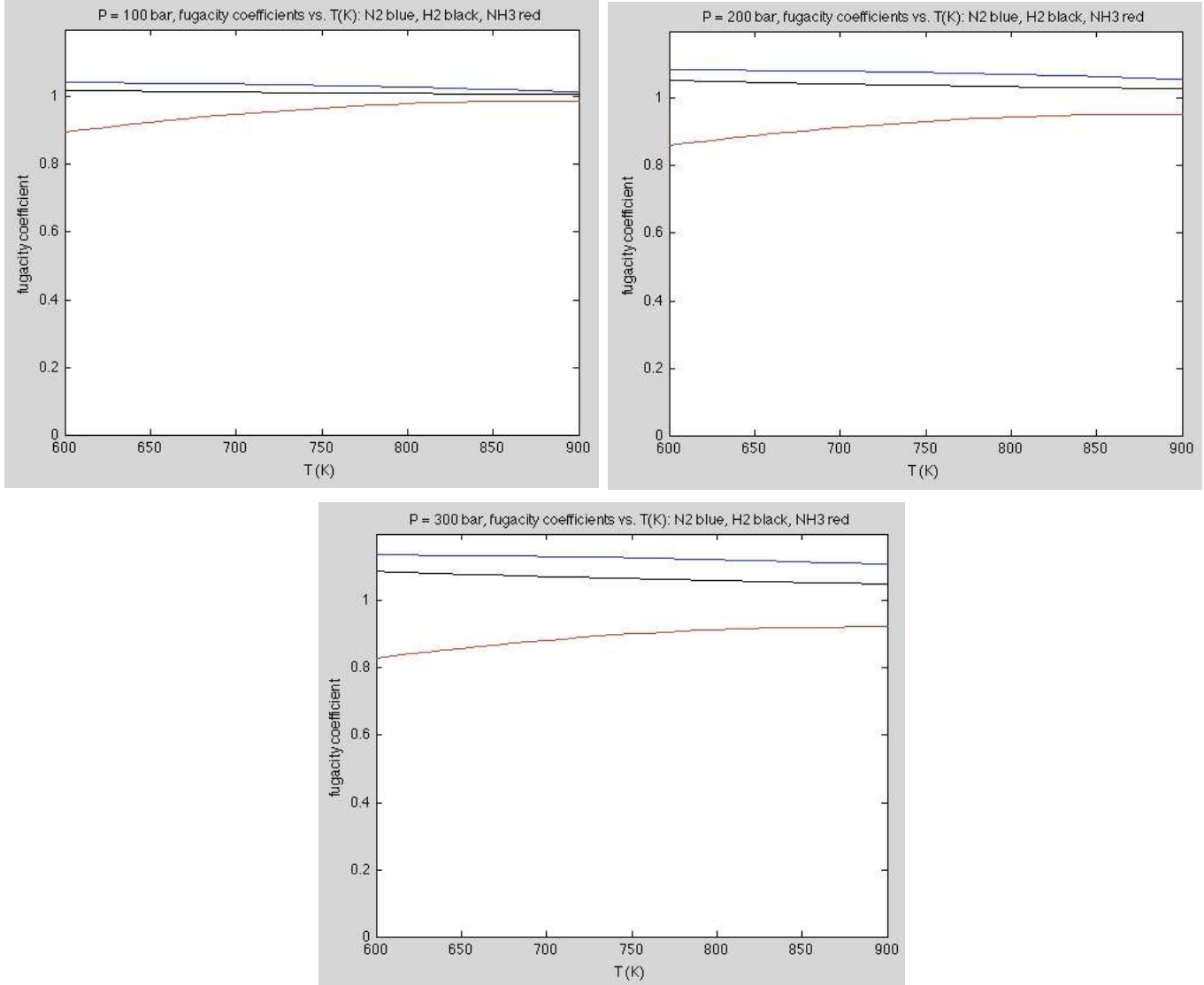
The figure below shows the ammonia percent for a stoichiometric mixture of H<sub>2</sub> and N<sub>2</sub> for the same conditions. The Matlab scripts used to produce these figures are listed below. Delete the page footer when copying.



For computing gas reaction equilibria, individual gas fugacities were used to compute  $K_\phi$ .

For ideal gases, fugacity equals partial pressure. For non-ideal gases, fugacity equals the fugacity coefficient times the partial pressure. An ideal gas has a fugacity coefficient value = 1.0. You could say that a gas with a fugacity coefficient of less than 1.0 has an "effective pressure" that is less than its partial pressure. Therefore, that gas will be present at equilibrium at a higher partial pressure than it would if it were to have ideal behavior.

The following figures show the fugacity coefficients for these gases vs. temperature at several total pressures. Note that the deviation from ideal gas behavior increases with increasing pressure.



### Listing of Matlab scripts - MAIN M-FILE ammo.m

```
% main file to compute NH3 equilibrium
% uses aequil.m

global Keq F0 P fchT fcntT fcaT

F0(1) = 0.5; % N2
F0(2) = 1.5; % H2
F0(3) = 0.0; % NH3

P = 300; % total pressure in bar
```

```

% G = Gibbs free energy change (kJ/mol) for 0.5 N2 + 1.5 H2 = NH3
G = [4.764 15.846 27.161 38.639 50.231 61.903];
T = [500 600 700 800 900 1000];

% fit G to a polynomial so can get values on finer T grid
coef = polyfit(T,G,2);
Tp = [500:10:1000];
Gp = polyval(coef,Tp);

% plot(T,G,'o',Tp,Gp) % plot to confirm fit
% title('delta-G vs. T')
% pause

% change to specified T range of 600-900 K
T = [600:10:900];
G = polyval(coef,T);

R = 0.00831; % kJ/mol-K

K = exp(-G./(R*T)); % equilibrium coefficient

% % compare to K from H.F. Rase, "Chemical Reactor Design for Process Plants,
% % vol. 2 Case Studies and Design Data", Wiley 1977, p. 63
log10K = -2.691122*log10(T) - 5.519265e-5*T + 1.848863e-7*T.^2 +...
2001.6 ./ T + 2.6899;
Krase = 10.^log10K;

% plot(T,K,'b',T,Krase,'k')
% title('K vs. T (black is from Rase case study)')
% pause

% compute fugacity coefficients to account for gas non-ideality
% from H.F. Rase, "Chemical Reactor Design for Process Plants,
% vol. 2 Case Studies and Design Data", Wiley 1977, p. 64
% P in bar, Pf below in atm (1 bar = 100 kPa = 0.98692 atm)
Pf = P*0.98692;
fch = exp(exp(-3.8402*T.^0.125+0.541)*Pf-exp(-0.1263*T.^0.5-15980)*Pf^2+...
300*(exp(-0.011901*T-5.491))*(exp(-Pf/300)-1)); % fch = fugacity coeffic of H2
fcn = 0.93431737 + 0.3101804e-3*T + 0.295896e-3*Pf - 0.2707279e-6*T.^2 +...
0.4775207e-6*Pf^2; % fcn = fugacity coefficient of N2
fca = 0.1438996 + 0.2028538e-2*T - 0.4487672e-3*Pf - 0.1142945e-5*T.^2 +...
0.2761216e-6*Pf^2; % fca = fugacity coefficient of ammonia, NH3
% these are now to be used with P in atm, adjust to use with P in bar
% aj = yj*fcj*P(atm) = yj*fcj*(atm/bar)*P(bar)
fch = fch*0.98692; % fugacity coefficient for use with P in bar
fcn = fcn*0.98692;
fca = fca*0.98692;

plot(T,fcn,'b',T,fch,'k',T,fca,'r')
title(['P = ' num2str(P) ...
' bar, fugacity coefficients vs. T(K): N2 blue, H2 black, NH3 red'])
ylabel('fugacity coefficient')
xlabel('T (K)')
axis([600 900 0 1.2])
pause

% ISE: 0.5 N2 + 1.5 H2 = NH3

% basis F0N2 = 0.5, F0H2 = 1.5
% extent can range from 0 to 1

for i = 1:31
    Keq = K(i); % K at T(i)
    fcnT = fcn(i); % N2 at T(i)

```

```

    fchT = fch(i); % H2
    fcaT = fca(i); % NH3
    e(i) = fminsearch('aequil',0,1);
end

F1 = F0(1)-0.5*e; % N2
F2 = F0(2)-1.5*e; % H2
F3 = F0(3)+e; % NH3
Ftot = F1+F2+F3;

X = (F0(1) - F1)/F0(1); % fractional conversion of N2

plot(T,X)
title(['P = ' num2str(P) ...
       ' bar, equilibrium fractional conversion of N2 vs. T (K), no NH3 in feed'])
axis([600 900 0 1])
ylabel('equilibrium fractional conversion of N2')
xlabel('T (K)')
pause

percentNH3 = 100*( F3./Ftot ); % for 3/1, H2/N2 feed with no NH3 in feed

plot(T,percentNH3)
title(['P = ' num2str(P)...
       ' bar, equilibrium mole percent NH3 vs. T (K)'])
axis([600 900 0 100])
ylabel('equilibrium mole percent NH3')
xlabel('T (K)')

```

### Listing of Matlab scripts - FUNCTION M-FILE aequil.m

```

function sse = aequil(e)

global Keq F0 P fchT fcnT fcaT

% ISE: 0.5 N2 + 1.5 H2 = NH3

F(1) = F0(1)-0.5*e(1); % N2
F(2) = F0(2)-1.5*e(1); % H2
F(3) = F0(3)+e(1); % NH3
Ftot = sum(F);

% compute activities for these gases from fugacity coeff, mol frac, and P
% P in bar and assume standard state = 1 bar

a(1) = fcnT*F(1)*P/Ftot; % chemical activity of N2
a(2) = fchT*F(2)*P/Ftot; % H2
a(3) = fcaT*F(3)*P/Ftot; % NH3

sse = ( Keq - a(3)/( a(1)^0.5 * a(2)^1.5 ) ).^2;

```