Chemical Reaction Equilibrium

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Step by step procedure to determine equilibrium conversion (X_{eq}) at given temperature (T) and pressure (P) using *Van't Hoff procedure.*

Reaction stoichiometry: $aA + bB \rightleftharpoons cC + dD$

1. Initial moles of A, B, C and D are n_{A0}, n_{B0}, n_{C0} and n_{D0} respectively.

2. Total moles is $N_0 = \sum n_{i0}$ where $i = A, B, C, D$

3. Change in moles due to reaction is $\triangle n = \sum v_i$ where $i = A, B, C, D$. Here v denotes the signed stoichiometric coefficient and
$$v_A = -a, v_B = -b, v_C = c, v_D = d$$

4. Standard temperature $T_0 = 25 \,°C = 298 \text{ K}$
   Standard pressure $P^0 = 1$ atm or 1 bar

5. Standard heat of reaction (in J/mol) $= \triangle H_R^\circ = \sum v_i \triangle H_{iF}^\circ$ where $\triangle H_{iF}^\circ$ is the standard heat of formation of $i \, (= A, B, C, D)$.

6. Standard entropy of reaction (in J/mol K) $= \triangle S_R^\circ = \sum v_i \triangle S_{iF}^\circ$ where $\triangle S_{iF}^\circ$ is the standard entropy of formation of $i \, (= A, B, C, D)$.

7. Standard gibbs energy of reaction (in J/mol) $= \triangle G_R^\circ = \triangle H_R^\circ - T_0 \triangle S_R^\circ$
   Note: If the standard gibbs energy of formation $\triangle G_{iF}^\circ$ are given, then $\triangle G_R^\circ$ can be directly obtained as $\triangle G_R^\circ = \sum v_i \triangle G_{iF}^\circ$.

8. Equilibrium constant K_0 at Standard temperature T_0 is given by $\triangle G_R^\circ = -R \, T_0 \, ln(K_0)$ where R is the universal gas constant. Find the value of K_0.
   <u>Note:</u> Ensure the unit consistancy of $\triangle G_R^\circ$ and R.

9. Van't Hoff expression to get equilibrium constant K at reaction temperature T is
$$ln\left(\frac{K}{K_0}\right) = -\frac{\triangle H_R^\circ}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]$$
   Find K.

10. Equilibrium constant (K_y) based on mole fraction at the reaction pressure (P) is
$$K_a = K = \frac{K_y P^{\triangle n}}{[P^\circ]^{\triangle n}}$$
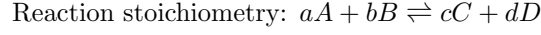   Find K_y.

11. Use mole balance table and get the expression for mole of key component.
    <u>Important note:</u> This is only the example of the form and not the exact expression.
$$K_y = \frac{\left(n_{C0} + \frac{c}{a}\,x\right)^c \left(n_{D0} + \frac{d}{a}\,x\right)^d}{\left(n_{A0} - x\right)^a \left(n_{B0} - \frac{b}{a}\,x\right)^b} \frac{1}{\left(N + \triangle n\,x\right)^{\triangle n}}$$

12. From above two steps, solve and get the value of for x. x is the extend of reaction/moles of key component reacted.

13. Equilibrium conversion (Assuming A is the key component) in percentage (%) is
$$\boxed{X_{eq} = \frac{x}{n_{A0}} * 100}$$

Step by step procedure to determine equilibrium conversion (X_{eq}) at given temperature (T) and pressure (P) using *Thermodynamic relation procedure.*

Reaction stoichiometry: $aA + bB \rightleftharpoons cC + dD$

1. Initial moles of A, B, C and D are n_{A0}, n_{B0}, n_{C0} and n_{D0} respectively.

2. Total moles is $N_0 = \sum n_{i0}$ where $i = A, B, C, D$

3. Change in moles due to reaction is $\triangle n = \sum v_i$ where $i = A, B, C, D$. Here v denotes the signed stoichiometric coefficient and
$$v_A = -a, v_B = -b, v_C = c, v_D = d$$

4. Standard temperature $T_0 = 25\ °C = 298\ K$
Standard pressure $P^0 = 1$ atm or 1 bar

5. Standard heat of reaction (in J/mol) $= \triangle H_R^\circ = \sum v_i \triangle H_{iF}^\circ$ where $\triangle H_{iF}^\circ$ is the standard heat of formation of i $(= A, B, C, D)$.

6. Standard entropy of reaction (in J/mol K) $= \triangle S_R^\circ = \sum v_i \triangle S_{iF}^\circ$ where $\triangle S_{iF}^\circ$ is the standard entropy of formation of i $(= A, B, C, D)$.

7. For the computation of specific heat contribution at reaction temperature (T), assume specific heat function of components to be given by polynomial as
$$C_{Pi} = a_{0i} + a_{1i}\ T + a_{2i}\ T^2 + a_{3i}\ T^3 \text{ where } i = A, B, C, D$$

Now compute $\begin{aligned} \triangle a_0 &= \sum v_i\ a_{0i} & \triangle a_1 &= \sum v_i\ a_{1i} \\ \triangle a_2 &= \sum v_i\ a_{2i} & \triangle a_3 &= \sum v_i\ a_{3i} \end{aligned}$

$$\triangle C_P = \triangle a_0 + \triangle a_1\ T + \triangle a_2\ T^2 + \triangle a_3\ T^3$$

$$\Rightarrow \int_{T_0}^{T} \triangle C_P\ dT = \int_{T_0}^{T} [\triangle a_0 + \triangle a_1\ T + \triangle a_2\ T^2 + \triangle a_3\ T^3]\ dT$$

$$= \triangle a_0\ [T - T_0] + \frac{\triangle a_1}{2}\ [T^2 - T_0^2] + \frac{\triangle a_2}{3}\ [T^3 - T_0^3] + \frac{\triangle a_3}{4}\ [T^4 - T_0^4]$$

Similarly,

$$\int_{T_0}^{T} \frac{\triangle C_P}{T}\ dT = \int_{T_0}^{T} \frac{[\triangle a_0 + \triangle a_1\ T + \triangle a_2\ T^2 + \triangle a_3\ T^3]}{T}\ dT$$

$$= \triangle a_0\ ln\frac{T}{T_0} + \triangle a_1\ [T - T_0] + \frac{\triangle a_2}{2}\ [T^2 - T_0^2] + \frac{\triangle a_3}{3}\ [T^3 - T_0^3]$$

Important note: Ensure unit consistency.

8. Enthalpy of reaction (in J/mol) at reaction temperature (T) is
$$\triangle H_R = \triangle H_R^\circ + \int_{T_0}^{T} \triangle C_P\ dT$$

9. Entropy of reaction (in J/mol K) at reaction temperature (T) is
$$\triangle S_R = \triangle S_R^\circ + \int_{T_0}^{T} \frac{\triangle C_P}{T}\ dT$$

10. Gibbs energy of reaction (in J/mol) at reaction temperature (T) is $\triangle G_R = \triangle H_R - T\ \triangle S_R$

11. Equilibrium constant K_a at reaction temperature T is given by $\triangle G_R = -R\ T\ ln(K_a)$ where R is the universal gas constant. Find the value of K_a.
Note: Ensure the unit consistancy of $\triangle G_R$ and R.

12. Equilibrium constant (K_y) based on mole fraction at the reaction pressure (P) is
$$K_a = K = \frac{K_y P^{\triangle n}}{[P^\circ]^{\triangle n}}$$

Find K_y.

13. Use mole balance table and get the expression for mole of key component.
    Important note: This is only the example of the form and not the exact expression.

$$K_y = \frac{\left(n_{C0} + \frac{c}{a} x\right)^c \left(n_{D0} + \frac{d}{a} x\right)^d}{\left(n_{A0} - x\right)^a \left(n_{B0} - \frac{b}{a} x\right)^b} \frac{1}{\left(N + \triangle n \, x\right)^{\triangle n}}$$

14. From above two steps, solve and get the value of for x. x is the extend of reaction/moles of key component reacted.

15. Equilibrium conversion (Assuming A is the key component) in percentage (%) is

$$\boxed{X_{eq} = \frac{x}{n_{A0}} * 100}$$

Problems involving Chemical Reaction Equilibrium

1. Reforming of natural gas is one of the important route to produce hydrogen in a petrochemical complex $(CH_4 + H_2O \rightleftharpoons CO + 3\,H_2)$. Find the equilibrium conversion at 1 bar pressure and 850 K, using the fundamental thermodynamic relation $(\triangle G_R = \triangle H_R - T \triangle S_R)$. The inlet feed contains the molar mixture of $1 : 1$ $CH_4 : H_2O$ only. The Specific heat capacities of components are given as

$$\frac{C_{P,CO}}{R} = 3.912 - 3.913 \times 10^{-3}\,T \qquad \frac{C_{P,H_2}}{R} = 2.883 + 3.681 \times 10^{-3}\,T$$

$$\frac{C_{P,CH_4}}{R} = 4.568 - 8.975 \times 10^{-3}\,T \qquad \frac{C_{P,H_2O}}{R} = 4.395 - 4.186 \times 10^{-3}\,T$$

Where R is the universal gas constant in appropriate units.

Solution: $X_{CO} = 69\%$

2. CO Methanation is a significant step in the production of synthetic natural gas $(CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O)$. Find the equilibrium conversion at 1 bar pressure and 800 K, using the fundamental thermodynamic relation $(\triangle G_R = \triangle H_R - T \triangle S_R)$. The inlet feed contains the molar mixture of $1 : 3$ $CO : H_2$ only. The Specific heat capacities of components are given as

$$\frac{C_{P,CO}}{R} = 3.912 - 3.913 \times 10^{-3}\,T \qquad \frac{C_{P,H_2}}{R} = 2.883 + 3.681 \times 10^{-3}\,T$$

$$\frac{C_{P,CH_4}}{R} = 4.568 - 8.975 \times 10^{-3}\,T \qquad \frac{C_{P,H_2O}}{R} = 4.395 - 4.186 \times 10^{-3}\,T$$

Where R is the universal gas constant in appropriate units.

Solution: $X_{CO} = 53.615\%$

3. Ammonia production from nitrogen and hydrogen is thermodynamically favorable at higher pressure and lower temperature. Compute the percentage equilibrium conversion (X_{N_2}) at the different operating conditions to illustrate the fact the lower temperature and higher pressure indeed favor ammonia production. The operating conditions are a) P = 1 bar, T = 650 K; b) P = 4 bar, T = 650 K and c) P = 4 bar, T = 500 K. Assume initial feed mixture consists of $1 : 3$ $N_2 : H_2$.

Solution:

Temperature, T (K)	Pressure, P (bar)	Equilibrium constant, K (-)	Equilibrium constant, K_y (-)	Percentage conversion, X_{N_2} (%)
650	1	0.00108	0.00108	2.67%
650	4	0.00108	0.017368944	7.6%
500	4	0.177328462	2.837255396	43.9%

4. Methanol production from syngas follows the reaction stoichiometry as $CO + 2\,H_2 \rightleftharpoons CH_3OH$. Determine the percentage equilibrium conversion of CO (X_{CO}) and the mole fraction of all the components at equilibrium at 1 bar pressure for an input mixture consisting of $1 : 3$ molar mixture of CO and H_2 at 400 K. Report conversion corrected to three decimal precision.
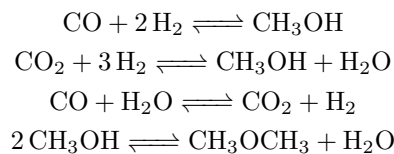
Solution:
$X_{CO} = 52\%$
Mole fraction of CO: $n_{CO} = 0.164$
Mole fraction of H_2: $n_{H_2} = 0.664$
Mole fraction of CH_3OH: $n_{CH_3OH} = 0.172$

5. Dimethyl ether synthesis from syngas mixture can be represented by the following reactions. Formulate generic expression to determine the composition of the mixture at equilibrium

$$CO + 2\,H_2 \rightleftharpoons CH_3OH$$
$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
$$2\,CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$

6. (a) CO Methanation is a significant step in the production of synthetic natural gas. The reaction stoichiometry is given by $CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O$. Find the equilibrium conversion at 1 bar pressure and 800 K using the Van't Hoff relation. The inlet feed contains the molar mixture of $1 : 5$ $CO : H_2$ only.

   (b) If Water gas shift reaction also occurs along with $CO + H_2O \rightleftharpoons CO_2 + H_2$, recompute the conversion of CO and the yield of methane. What is the percentage decrease in the yield of methane.

Additional Data

Component	Standard enthalpy of formation (kJ/mol)	Standard entropy of formation (kJ/mol K)
CH_3OH	-200.94	0.23988
CH_4	-74.52	0.18627
CO	-110.53	0.197556
CO_2	-393.51	0.213677
H_2	0	0.130571
H_2O	-241.814	0.188724
N_2	0	0.1915
NH_3	-45.898	0.19266