
Chemical Engineering Thermodynamics CHE F213

Chemical-Reaction Equilibria

Outline



- Introduction
- Reaction co-ordinate
- Multiple reaction stoichiometry
- Standard Gibbs free energy and Standard Enthalpy change for a reaction
- Equilibrium constant (K)
- Relation of equilibrium constant to composition
- Effect of temperature and pressure on K

Chemical reaction Equilibria

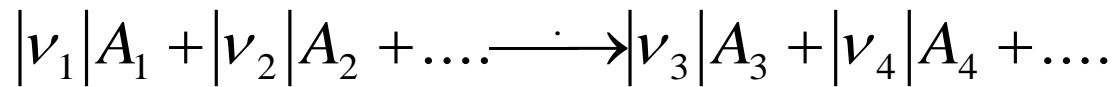


- ❑ Reactor: Heart of chemical plant : Raw materials get converted to product
- ❑ Chemical Engineers design reactors
- ❑ Need to understand degree of conversion at equilibrium
- ❑ Thermodynamics (equilibrium) and Kinetics (rate) then go hand in hand
- ❑ Equilibrium conversion: $f(T, P \text{ and composition})$
- ❑ Maximizing yield from a reactor under optimum pressure and temperature is the objective

Reaction coordinate



- The general chemical reaction is written as:



where $|\nu_i|$ is stoichiometric coefficient (sign convention + for product, - for reactant and 0 for inert) and A_i is chemical formula

- As the reaction progresses, the change in the number of moles of species present in the reaction is directly proportional to their respective stoichiometric numbers

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} \equiv d\varepsilon$$

- Here ε represents the amount of reaction and is called **reaction coordinate**, characterize the extent/degree of reaction

Reaction coordinate



$$dn_i = v_i d\varepsilon \quad (i = 1, 2, \dots, N)$$

Integrating above eqn. from an initial unreacted state where $\varepsilon = 0$ and $n_i = n_{i0}$ to a state reached after an arbitrary amount of reaction gives,

$$\int_{n_{i0}}^{n_i} dn_i = v_i \int_0^{\varepsilon} d\varepsilon$$

$$n_i = n_{i0} + \varepsilon v_i$$

$$\text{total number of moles } n = \sum n_{i0} + \varepsilon \sum v_i$$

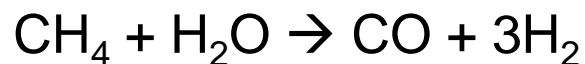
$$n_o = \sum n_{i0} \text{ \& } v = \sum v_i$$

$$y_i = n_i/n = (n_{i0} + v_i \varepsilon) / (n_o + v \varepsilon)$$

Illustration 1 (Example 13.1)



The following reaction takes place in a system containing 2 moles of methane, 1 mol water, 1 mol CO and 4 mol hydrogen



- Identify the mol numbers
- Identify the total number of moles
- Identify the stoichiometric number of each species
- Identify the sum of the stoichiometric number
- If the extent of reaction is ε , what is the mole fraction in terms of ε ?

Multi-reaction Stoichiometry



For two or more independent reactions, subscript j serves as reaction index

$$\text{For species } i : n_i = n_{i0} + \sum v_{i,j} \varepsilon_j$$

$$\text{Total number of moles } n = n_o + \sum v_j \varepsilon_j$$

$$n_o = \sum n_{i0} \text{ \& } v = \sum v_{i0}$$

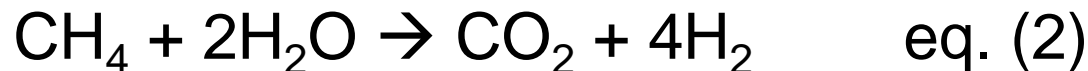
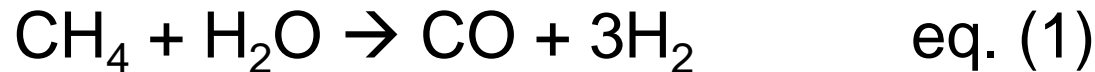
$$y_i = n_i/n = (n_{i0} + \sum v_{i,j} \varepsilon_j) / (n_o + \sum v_j \varepsilon_j)$$

Here $v_j = \sum v_{i,j}$ for a single reaction

Illustration 2 (Example 13.3)



A system initially charged with 2 mol of CH_4 and 3 mol of water is undergoing the following reaction



If the extent of reaction is ε_1 and ε_2 , for reaction 1 and 2 respectively, determine expressions for the y_i , as functions of ε_1 and ε_2 .

Equilibrium criterion for a chemical reaction



- A Chemical reaction must proceed in the direction of decreasing total Gibbs free energy (G^t) .
- At equilibrium state, $(dG^t)_{T,P} = 0$

$$(dG)_{T,P} = 0 = \sum \mu_i dn_i = \sum \mu_i \nu_i d\varepsilon = 0$$

CRITERION FOR EQUILIBRIUM

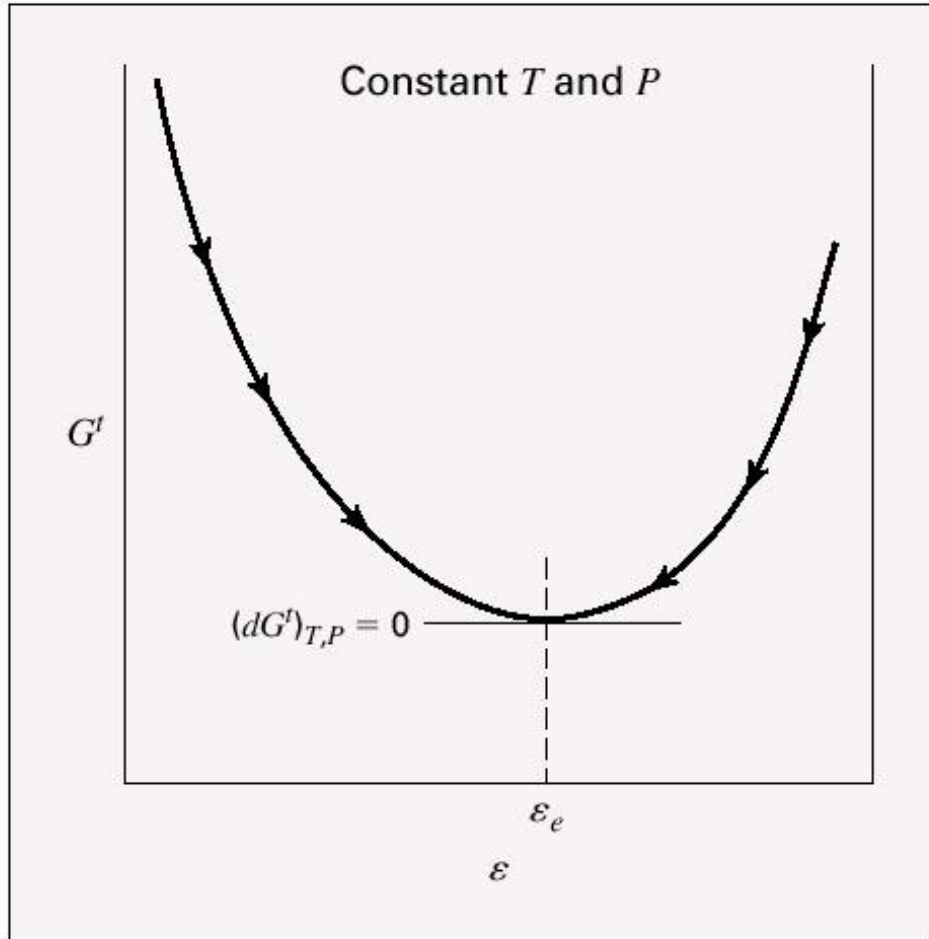


Figure 13.1: The total Gibbs energy in relation to the reaction coordinate.

The standard Gibbs-Energy change and the Equilibrium constant



The fundamental property relation for single-phase systems, provides an expression for the total Gibbs energy

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

For changes in the mole numbers n_i , as the result of a single chemical reaction

$$d(nG) = (nV)dP - (nS)dT + \sum_i \nu_i \mu_i d\varepsilon$$
$$\text{or..} \sum_i \nu_i \mu_i = \left[\frac{\partial(nG)}{\partial \varepsilon} \right]_{T,P} = \left[\frac{\partial(G^t)}{\partial \varepsilon} \right]_{T,P}$$

Thus the quantity $\sum \nu_i \mu_i$ represent the change in total Gibbs energy of the system with respect to the reaction coordinate at T,P.

Equilibrium Constant K



A criterion of chemical-reaction equilibrium is

$$\sum_i \nu_i \mu_i = 0$$

Recall the definition of the fugacity of a species in solution:

$$\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

The Gibbs free energy of species i in standard state (1 atm and 25°C)

$$G_i^0 = \Gamma_i(T) + RT \ln f_i^0$$

The difference between the two equations is

$$\mu_i - G_i^0 = RT \ln \frac{\hat{f}_i}{f_i^0}$$

Put μ_i expression from above equation to reaction equilibrium criteria

$$\sum \mu_i \nu_i = 0$$

Equilibrium Constant

$$\sum_i \nu_i \left[G_i^0 + RT \ln \frac{\hat{f}_i}{f_i^0} \right] = 0 \quad \Rightarrow \quad \ln \prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = \frac{-\sum_i \nu_i G_i^0}{RT}$$

Introducing a new term equilibrium constant K as:

$$\prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = K$$

$$K \equiv \exp \left(\frac{-\Delta G^0}{RT} \right) \quad \text{or} \quad \ln K = \left(\frac{-\Delta G^0}{RT} \right)$$

where $\Delta G^0 = \sum_i \nu_i G_i^0$

Standard Gibbs-energy change of reaction

ΔG^0 is pure species property at fixed pressure, it depends only on temperature and hence K are also functions of temperature only.

Standard state Gibbs Energy from Enthalpy



Standard property (M) change of reaction is defined as

$$\Delta M^o \equiv \sum_i \nu_i \Delta M^o$$

For example,

$$\Delta H_{rxn}^o(T = 25^oC) = \sum_i \nu_i \Delta H_{f_i}^o(T = 25^oC) \quad \text{and} \quad \Delta C_P^o(T = 25^oC) = \sum_i \nu_i C_{P_i}^o$$

The relation between the standard heat of reaction ΔH_i^o and the standard Gibbs energy change of reaction for species i in standard state :

$$\Delta H_i^o = -RT^2 \frac{d(\Delta G_i^o / RT)}{dT}$$

$$\Delta H^o = -RT^2 \frac{d(\Delta G^o / RT)}{dT}$$

Effect of temperature on K



Standard Heat (enthalpy) of reaction and Standard Gibbs free energy change are related by property relation (at constant P and composition)

$$\frac{d(\Delta G^0 / RT)}{dT} = - \frac{\Delta H_{rxn}^0}{RT^2}$$

In terms of equilibrium constant

$$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^0}{RT^2}$$

- The effect of temperature on the equilibrium constant K is determined by the sign of ΔH_{rxn}^0

$\Delta H_{rxn}^0 > 0$ (Endothermic reaction) : increase in T increases K

$\Delta H_{rxn}^0 < 0$ (Exothermic reaction) : increase in T decreases K

Effect of temperature on K

$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^0}{RT^2}$ can be integrated between two temperature

T_1 and T_2 :

$$\ln \frac{K(T_2)}{K(T_1)} = \int_{T_1}^{T_2} \frac{\Delta H_{rxn}^0(T)}{RT^2} dT$$

If ΔH_{rxn}^0 is constant over a temperature range, integration of the above equation for two temperature limits, result

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

PLOT OF $\ln K$ vs $1/T$ will be a straight line

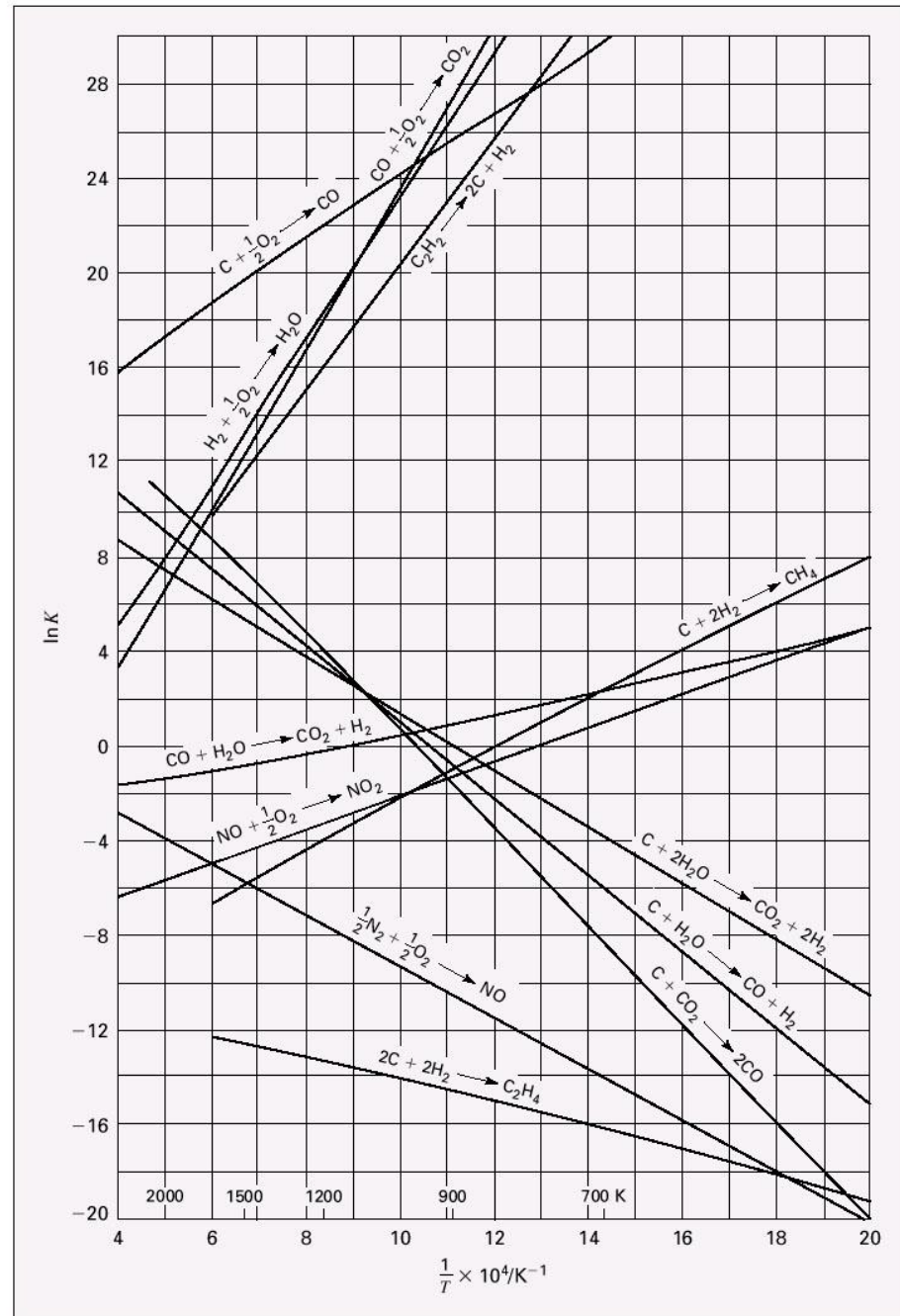


Figure 13.2: Equilibrium constants as a function of temperature.

Calculation of effect of temperature on K



The development of the effect of temperature on equilibrium constant is based on definition of G_i°

$$G_i^\circ = H_i^\circ - TS_i^\circ$$

Multiplication by ν_i and summation over all species gives

$$\sum_i \nu_i G_i^\circ = \sum_i \nu_i H_i^\circ - T \sum_i \nu_i S_i^\circ$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The standard heat of reaction is related to temperature (T)

$$\Delta H^\circ(T) = \Delta H_0^\circ(T = 25^\circ\text{C}) + R \int_{T_0}^T \frac{\Delta C_P^\circ}{R} dT$$

$$-\ln K = \frac{\Delta G^\circ(T)}{RT} = \frac{\Delta G_0^\circ - \Delta H_0^\circ(T = 25^\circ\text{C})}{RT_0} + \frac{\Delta H_0^\circ}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_P^\circ}{R} dT - \int_{T_0}^T \frac{\Delta C_P^\circ}{R} \frac{dT}{T}$$

Relation of Equilibrium constants to composition



•Gas Phase reactions

$$\prod_i \left(\frac{\hat{f}_i}{P^o} \right)^{v_i} = K \quad \text{Here } P_0 \text{ is standard state pressure of 1 bar}$$

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

For ideal solution case :

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

For low pressures and/or high temperatures, the equilibrium mixture behaves as an ideal gas

$$\prod_i (y_i)^{v_i} = \left(\frac{P}{P_0} \right)^{-\nu} K \quad (13.28)$$

Effect of pressure and temperature on equilibrium constant



$$\prod_i (y_i)^{v_i} = \left(\frac{P}{P_0} \right)^{-\nu} K \quad (13.28)$$

- Equation shows that an increase in K at constant P result in increase in left term, which implies a shift of reaction to the right and an increase in ε_e and vice versa.
- If the total stoichiometric number ν is negative, an increase in P at constant T causes an increase in left side term, implying a shift of reaction to the right and an increase in ε_e and vice versa.

*** Validates Le Chatelier's Principle

Liquid phase reaction

For a reaction occurring in the liquid phase,

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

$$\hat{f}_i = \gamma_i x_i f_i \quad \Rightarrow \quad \frac{\hat{f}_i}{f_i^o} = \gamma_i x_i \left(\frac{f_i}{f_i^o} \right)$$

For pure liquid i,

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

As V_i changes little with change in pressure for liquids

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

Equilibrium Constant for Liquid Phase Reaction



General expression for liquid phase equilibrium constant

$$\prod_i (x_i \gamma_i)^{\nu_i} = K \exp \left[\frac{(P^\circ - P)}{RT} \sum_i (\nu_i V_i) \right]$$

For low to moderate pressures, exponential term is unity

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

If the equilibrium mixture is an ideal solution, then γ_i is unity

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

This simple equation is known as ***law of mass action***.

Equilibrium conversion for single reaction



For gas phase reaction:

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

For liquid phase reaction

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

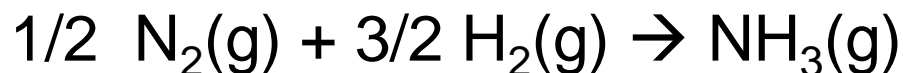
Relation of reaction extent to mole fractions

$$y_i = n_i/n = (n_{i0} + \sum \nu_{i,j} \epsilon_j) / (n_0 + \sum \nu_j \epsilon_j)$$

Illustration (Problem 13.9)



For the ammonia synthesis reaction written as



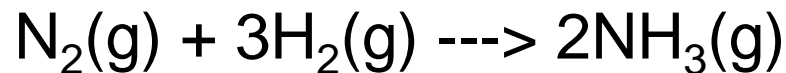
with 0.5 mol N_2 and 1.5 mol H_2 , as the initial amounts of reactants and with the assumption that the equilibrium mixture is an ideal gas, show that

$$\varepsilon_e = 1 - \left(1 + 1.299K \frac{P}{P^o} \right)^{-1/2}$$

Problems



Example 1. Write the equilibrium constant expression for the reaction in terms of partial pressures (assume ideal gas mixture)



Solution. All species are gases, so we use their partial pressures

$$K_{\text{eq}} = P_{\text{NH}_3}^2 / P_{\text{H}_2}^3 P_{\text{N}_2}$$

Equilibrium constant (Hess law)



Rule 1

Multiplication of a reaction by a constant

- If all of the stoichiometric coefficients of an equation are multiplied by the same constant, the new equilibrium constant expression is obtained by raising the old one to a power equal to the constant ($K_2 = K_1^n$)

Rule 2

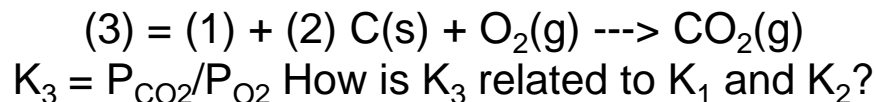
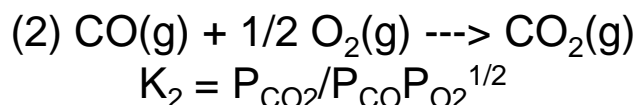
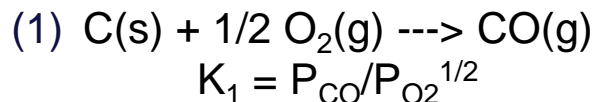
Reversing a reaction. If a reaction is reversed (turned around), its equilibrium constant is reciprocated (inverted).

Problems



Combining reactions by addition or subtraction. We use Hess's Law to obtain a desired reaction by adding (subtracting) two or more other reactions. How is K_{eq} for the sum related to the K_{eq} 's of the combined reactions? Again, example illustrates this clearly.

Example 12-6. The third reaction below can be obtained by adding the first two reactions.



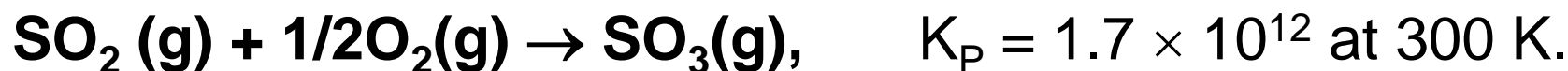
Solution. Inspection of the equilibrium constant expressions shows that K_3 is the product of K_1 and K_2 . Generalizing, when two reactions are added to give a third, their K_{eq} 's must be multiplied to obtain K_{eq} for the third:

$$(3) = (1) + (2) \quad K_3 = K_1 K_2$$

Illustration



For the reaction represented by



Calculate K_p for the following reactions at 300K

- $\text{SO}_3(\text{g}) \rightarrow \text{SO}_2(\text{g}) + 1/2\text{O}_2(\text{g})$
- $2\text{SO}_3(\text{g}) \rightarrow 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g})$
- $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

Solution

$$K_{P(i)} = \frac{p_{\text{SO}_2} \cdot p_{\text{O}_2}^{1/2}}{p_{\text{SO}_3}}$$

This is reverse of reaction (A). Therefore

$$K_{P(i)} = \frac{1}{K_P} = \frac{1}{1.7 \times 10^{12}} = 0.588 \times 10^{-12}$$

Consider reaction (ii). This equation has been obtained when equation (i) is multiplied by 2. Therefore

$$K_{P(ii)} = \frac{p_{\text{SO}_2}^2 p_{\text{O}_2}}{p_{\text{SO}_3}^2} = K_{P(i)}^2 = 0.334 \times 10^{-24}$$

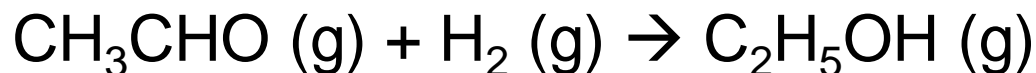
For reaction (iii)

$$\begin{aligned} K_{P(iii)} &= \frac{p_{\text{SO}_3}^2}{p_{\text{SO}_2}^2 \cdot p_{\text{O}_2}} = K_P^2 = \frac{1}{K_{P(i)}^2} = \frac{1}{K_{P(ii)}} \\ &= 2.89 \times 10^{24}. \end{aligned}$$

Illustration (Problem 13.13)



The following reaction reaches equilibrium at 350°C and 3 bar:



If the system initially contains 1.5 mol H₂ and 1 mol of acetaldehyde, what is the composition of the system at equilibrium? What would be the effect of reducing the pressure to 1 bar ? Assume ideal gases.

Solution



$\Delta G_{298.15K}$ -39630J/mol

$\Delta H_{298.15K}$ -68910J/mol

C_p/R

ΔA -1.424

ΔB 0.001601

ΔC 0.000000146

ΔD -8300

T 623.15K

P 3 bar

p_1 11.81207616

p_2 -13.3008572

p_3 -0.36451219

p_4 -0.54357444

ΔG_T -1.30971878

K 3.705131616

$$-\ln K = \frac{\Delta G^o(T)}{RT} = \frac{\Delta G_0^o - \Delta H_0^o(T = 25^o C)}{RT_0}$$

$$+ \frac{\Delta H_0^o}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_P^o}{R} dT - \int_{T_0}^T \frac{\Delta C_P^o}{R} \frac{dT}{T}$$

$$-\ln K = P1 + P2 + p3 - p4$$