

Example 8.1

Consider the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	a	$b \times 10^3$	$c \times 10^6$	$d \times 10^9$	$e \times 10^{-5}$
C_2H_4	20.691	205.346	- 99.793	18.825	-
H_2O	4.196	154.565	- 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

From standard tables $\Delta H_{R,298}^0 \approx -52.7$ KJ; $\Delta G_{R,298}^0 = 14.5$ KJ

$$\text{Now } \Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^T \Delta C_p^0 dT \text{ ----- (A)}$$

$$\Delta C_p^0 = \sum \alpha_i C_{p,i}^0 = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3 + \Delta e/T^2 \text{ ----- (B)}$$

Where:

$$\Delta a = \sum \alpha_i a_i, \Delta b = \sum \alpha_i b_i, \text{ etc}$$

$$\text{For example } \Delta a = 20.691 - 4.196 - 28.850 = -12.355$$

$$\Delta b = (205.346 - 154.565 - 12.055) \times 10^{-3} = 3.8726 \times 10^{-2}$$

$$\text{Similarly } \Delta c = -1.8717 \times 10^{-5}; \Delta d = 2.012 \times 10^{-9}; \Delta e = -1.006 \times 10^{-5}$$

Putting B in A and integrating A we get:

$$\Delta H_T^0 = -50.944(KJ) - 12.355T + \frac{3.8726 \times 10^{-2}}{2} T^2 - \frac{1.8717 \times 10^{-5}}{3} T^3 + \frac{2.012 \times 10^{-9}}{4} T^4 + 1.006 \times 10^5 / T \text{(C)}$$

$$\text{By Vant Hoff equation: } \frac{d(\Delta G_T^0 / RT)}{dT} = - \frac{\Delta H_T^0}{RT^2}$$

$$\therefore \frac{\Delta G_T^0}{RT} - \frac{\Delta G_{298}^0}{R(298)} = - \int_{298}^T \frac{\Delta H_T^0}{RT^2} dT \text{ ----- D}$$

We already know ΔH_T^0 from (C); putting C in D and integrating we obtain:

$$\Delta G_T^0 = -50.944 + 12.355T \ln T - \frac{3.8726 \times 10^{-2}}{2} T^2 + \frac{1.8718 \times 10^{-5}}{6} T^3 - \frac{2.012 \times 10^{-9}}{12} T^4 + \frac{1.006 \times 10^5}{2T} + 56.681T$$

Putting $T=500\text{K}$, $\Delta G_T^0 = 11.43\text{kJ}$

Example 8.2

Consider the following reaction: $A(g) + B(g) = C(g) + 3D(g)$ $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$

Initially the following number of moles are introduced in the reactor. Obtain the mole fraction expressions in terms of reaction coordinate.

$$n_{0,A} = 2 \text{ mol}, n_{0,B} = 1 \text{ mol}, n_{0,C} = 1 \text{ mol}, n_{0,D} = 4 \text{ mol}$$

$$\alpha \sum \alpha_i = -i = -1-1+1+3 = 2$$

$$n_0 = \sum_i n_{i_0} = 2 + 1 + 1 + 4 = 8$$

$$y_i = \frac{n_i}{n} = \frac{n_{i_0} + \alpha_i \xi}{n_0 + \alpha \xi}$$

$$\therefore \therefore y_A = \frac{2-\xi}{8+2\xi}; \quad y_B = \frac{1-\xi}{8+2\xi}; \quad y_C = \frac{1+\xi}{8+2\xi}; \quad y_{H_2} = \frac{4+\xi}{8+2\xi}$$

Example 8.3

Consider the following simultaneous reactions. Express the reaction mixture composition as function of the reaction co-ordinates. All reactants and products are gaseous.



Initial number of moles:

$$n_{0,A} = 2 \text{ mol}; \quad n_{0,B} = 3 \text{ mol}$$

Let the reaction co-ordinates for each reaction be ξ_1 and ξ_2 respectively.

j	A	B	C	D	E	$\alpha_j = \sum \alpha_{i,j}$
1	-1	-1	1	3	0	2
2	-2	-2	0	4	1	2

$$y_i = \frac{n_{i_0} + \sum_j \alpha_{i,j} \xi_j}{n_0 + \sum_j \alpha_j \xi_j}; \quad n_0 = 2+3 = 5$$

$$\therefore y_A = \frac{2-\xi_1-\xi_2}{5+2\xi_1+2\xi_2}; \quad y_B = \frac{3-\xi_1-2\xi_2}{5+2\xi_1+2\xi_2}; \quad y_C = \frac{\xi_1}{5+2\xi_1+2\xi_2}$$

$$y_D = \frac{3\xi_1 + 4\xi_2}{5 + 2\xi_1 + 2\xi_2}; y_E = \frac{\xi_2}{5 + 2\xi_1 + 2\xi_2}$$

Example 8.4

Consider the reaction : $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the equilibrium constant, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

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Putting $T=500\text{K}$, $\Delta G_T^0 = 11.43\text{kJ}$

Hence $K_{500} = \exp [-1143/8.314 \times 1000] = 0.064$

Example 8.5

Consider the reaction: $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{\text{ig}} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

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Putting $T=500K$, $\Delta G_T^0 = 11.43KJ$

Hence $K_{500} = \exp [-1143/8.314 \times 1000] = 0.064$

$$\alpha = \sum \alpha_i = 1 - 1 - 1 = -1$$

$\therefore K = K_\phi K_y P^\alpha$; $K_\phi = 1$ (since ideal gas assumption is made)

$$P = 40 \text{ bar}$$

Component	n_{i0}	$n(\text{exit})$	$y_i(\text{exit})$
C ₂ H ₄	1	$1 - \epsilon$	$(1 - \epsilon)/(2 - \epsilon)$
H ₂ O	1	$1 - \epsilon$	$(1 - \epsilon)/(2 - \epsilon)$
C ₂ H ₅ OH	0	ϵ	$(\epsilon)/(2 - \epsilon)$

$$n_t (\text{at exit}) = 2 - \epsilon$$

$$\therefore K = K_y = y_{C_2H_5OH} / y_{C_2H_4} y_{H_2O} = \frac{\xi/(2 - \xi)}{\{(1 - \xi)/(2 - \xi)\}^2} = \frac{\xi(2 - \xi)}{(1 - \xi)^2}$$

$$\text{Now } K = K_\phi K_y P^\alpha = (1) K_y P^{-1}$$

$$\therefore K_y = 40K; K_y = \xi(2 - \xi)/(1 - \xi)^2$$

$$\therefore K_y = \frac{\xi(2 - \xi)}{(1 - \xi)^2} = 40 \times K_{500} = 40 \times 0.064 = 2.56$$

On solving $\xi = 0.47$

$$\text{Thus } y_{C_2H_4} = (1 - \xi)/(2 - \xi) = 0.3464 = y_{H_2O}$$

$$y_{C_2H_5OH} = \xi/(2 - \xi) = 0.3072$$

Example 8. 6

The following two independent reactions occur in the steam cracking of methane at 1000 K and 1 bar: $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$; and $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$. Assuming ideal gas behaviour determine the equilibrium composition of the gas leaving the

reactor if an equimolar mixture of CH₄ and H₂O is fed to the reactor, and that at 1000K, the equilibrium constants for the two reactions are 30 and 1.5 respectively.

Let ξ_1 and ξ_2 be the reaction co-ordinate for the two reactions, we have

Comp	n_{i0}	n_{exit}	y_{exit}
CH ₄	1	$1 - \xi_1$	$(1 - \xi_1) / 2(1 + \xi_1)$
H ₂ O	1	$1 - \xi_1 - \xi_2$	$(1 - \xi_1 - \xi_2) / 2(1 + \xi_1)$
CO	0	$\xi_1 - \xi_2$	$(\xi_1 - \xi_2) / 2(1 + \xi_1)$
CO ₂	0	ξ_2	$\xi_2 / 2(1 + \xi_1)$
H ₂	0	$3 \xi_1 + \xi_2$	$(3 \xi_1 + \xi_2) / 2(1 + \xi_1)$

Total moles at equilibrium: $2(1 + \xi_1)$

$K = K_\phi K_y P^\alpha$ (for each reaction); $K_\phi = 1.0$ (ideal gas assumption); $P = 1$ bar

$$\text{Thus } K_1 = \frac{\left[\frac{(\xi_1 - \xi_2)}{2(1 + \xi_1)} \right] \left[\frac{(3\xi_1 + \xi_2)}{2(1 + \xi_1)} \right]^3}{\left[\frac{(1 - \xi_1)}{2(1 + \xi_1)} \right] \left[\frac{(1 - \xi_1 - \xi_2)}{2(1 + \xi_1)} \right]} = \frac{(\xi_1 - \xi_2)(3\xi_1 + \xi_2)^3}{4(1 + \xi_1)^2(1 - \xi_1)(1 - \xi_1 - \xi_2)} = 30 \quad \text{..... A}$$

$$\text{Similarly } K_2 = \frac{(3\xi_1 + \xi_2)\xi_2}{(\xi_1 - \xi_2)(1 - \xi_1 - \xi_2)} = 1.5 \quad \text{..... B}$$

A and B needs to be solved simultaneously; a simple way to do this is to

- (i) Assume ξ_2 , calculate ξ_1 using B
- (ii) Use ξ_2 and ξ_1 in A to check if $K_1 = 30$
- (iii) If $K_1 \neq 30$, assume new ξ_2 and go to step 1

Using the above algorithm, one finally obtains: $\xi_1 = 0.7980$, $\xi_2 = 0.0626$.

Thus: $y_{\text{CO}_2} = 0.0174$, $y_{\text{CH}_4} = 0.0562$, $y_{\text{H}_2\text{O}} = 0.0388$, $y_{\text{CO}} = 0.2045$, $y_{\text{H}_2} = 0.6831$

Example 8.7

The gas n-pentane (1) is known to isomerise into neo-pentane (2) and iso-pentane (3) according to the following reaction scheme: $P_1 \rightleftharpoons P_2$; $P_2 \rightleftharpoons P_3$; $P_3 \rightleftharpoons P_1$. 3 moles of

pure n-pentane is fed into a reactor at 400° K and 0.5 atm. Compute the number of moles of each species present at equilibrium.

Species	ΔG_f^0 at 400° K (Cal/mol)
P ₁	9600
P ₂	8900
P ₃	8200

We use here the method of undetermined Lagrangian Multipliers.

The set of equation to be solved are:

$$A_C = 15, A_H = 36$$

$$\text{For P}_1: \frac{9600}{RT} + \ln \left(\frac{n_1}{\sum n_i} \right) + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$$

$$\text{For P}_2: \frac{8900}{RT} + \ln \left(\frac{n_2}{\sum n_i} \right) + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$$

$$\text{For P}_3: \frac{8200}{RT} + \ln \left(\frac{n_3}{\sum n_i} \right) + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$$

$$\text{Atomic mass balance for C: } 5(n_1 + n_2 + n_3) = 15$$

$$\text{For H: } 12(n_1 + n_2 + n_3) = 36$$

$$n_1 + n_2 + n_3 = 10$$

$$\text{Alternately: } \frac{9600}{RT} + \ln y_1 + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0 \dots\dots\dots (A)$$

$$\frac{8900}{RT} + \ln y_2 + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0 \dots\dots\dots (B)$$

$$T = 400K$$

$$\frac{8200}{RT} + \ln y_3 + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0 \dots\dots\dots (C)$$

$$\text{and } y_1 + y_2 + y_3 = 1 \dots\dots\dots (D)$$

It follows from (A) – (C), $y_2 / y_1 = 2.41$; $y_3 / y_2 = 2.41$

Using eqn. (D) $y_1 = 0.108$, $y_2 = 0.29$, $y_3 = 0.63$

Example 8.8

Consider the liquid phase reaction: $A(l) + B(l) \rightarrow C(l) + D(l)$. At 50°C , the equilibrium constant is 0.09. Initial number of moles, $n_{A,0} = 1$ mole; $n_{B,0} = 1$ mol Find the equilibrium conversion. Assume ideal solution behaviour.

$$\therefore K = \underbrace{\prod_i (x_i \gamma_i)^{\gamma_i} \exp \left\{ \frac{(P-1) \sum \gamma_i V_i}{RT} \right\}}_{1.0}$$

Also, $\gamma_i = 1$ (ideal solution)

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

$$x_A = x_B = (1-\xi)/2; \quad x_C = x_D = \xi/2$$

$$\therefore K = x_C x_D / x_A x_B = [\xi/(1-\xi)]^2$$

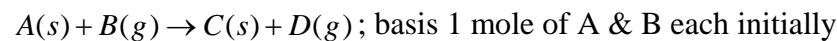
$$\Rightarrow 0.09 = [\xi/(1-\xi)]^2$$

$$\text{Thus, } \xi_e = 0.23$$

Example 8.9

Consider the following reaction: $A(s) + B(g) \rightarrow C(s) + D(g)$. Determine the equilibrium fraction of B which reacts at 500°C if equal number of moles of A and B are introduced into the reactor initially. The equilibrium constant for the reaction at 500°C is 2.0.

The reaction is:



$$K = \hat{a}_C \hat{a}_D / \hat{a}_A \hat{a}_B$$

$$\text{For solids: } \hat{a} = 1$$

Thus:

$$K = \hat{a}_D / \hat{a}_B = K_\phi K_y P^\alpha; \alpha = 0, \text{ and } K_\phi = 1$$

$$\therefore K = K_y$$

If one assumes equimolar feed of reactants:

$$y_B = (1-\xi); \quad y_D = \xi$$

$$\therefore K = K_y = 2.0 = \frac{\xi}{1-\xi} \Rightarrow \xi = 0.67$$

Thus 67% of B reacts.